

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C10L 1/32</b>	<b>A2</b>	<b>(11) International Publication Number:</b> <b>WO 95/20637</b> <b>(43) International Publication Date:</b> 3 August 1995 (03.08.95)
<b>(21) International Application Number:</b> PCT/IT95/00009 <b>(22) International Filing Date:</b> 27 January 1995 (27.01.95) <b>(30) Priority Data:</b> ME94A000002 31 January 1994 (31.01.94) IT <b>(71) Applicant (for all designated States except US):</b> MEG S.N.C. DI SCOPELLITI SOFIA & C. [IT/IT]; Via Marco Polo, 73 G/B/9, I-98100 Messina (IT). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> FERRARA, Marcello [IT/IT]; Via Marco Polo, 73 G/B/9, I-98100 Messina (IT). <b>(74) Agent:</b> MASCIOLI, Alessandro; A.N.D.I. - Associazione Nazionale Degli Inventori, Via Urbana, 20, I-00184 Roma (IT).		<b>(81) Designated States:</b> AU, CA, JP, KR, MX, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> HYDROCARBON OIL, AQUEOUS, FUEL AND ADDITIVE COMPOSITIONS  <b>(57) Abstract</b>  The present invention relates to processes and additive compositions capable of performing at least one of the following: a) stabilizing asphaltenes flocculated and/or precipitated in a petroleum product (as a crude oil, a residue or a fuel oil), rendering thus possible its blending with other petroleum products or its processing or its combustion; b) reducing fouling in petroleum apparatuses; c) achieving yield increase in petroleum refining and/or petrochemical operations; d) reducing particulate and/or SO <sub>x</sub> and/or NO <sub>x</sub> emissions during combustion of fuels; e) reducing fouling and/or coke formation in catalysts; f) favouring cleaning and/or decoking of petroleum apparatuses; g) reducing fouling arising from diesel and biodiesel fuels.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

## HYDROCARBON OIL-AQUEOUS FUEL AND ADDITIVE COMPOSITIONS.

5 The present invention relates to processes and additives compositions capable of performing at least one of the following: a) stabilizing asphaltenes flocculated and/or precipitated in a petroleum product (as a crude oil, a residue or a fuel oil), rendering thus possible its blending with other petroleum products or its processing or its combustion ; b) reducing fouling in petroleum apparatuses; c) achieving yield increase in petroleum refining and/or petrochemical operations; d) 10 reducing particulate and/or soot and/or SO<sub>x</sub> and/or NO<sub>x</sub> emissions during combustion of fuels; e) reducing fouling and/or coke formation in catalysts; f) favouring cleaning and/or decoking of petroleum apparatuses; g) reducing fouling arising from diesel and biodiesel fuels.

15 Additive compositions can be dispersed in new types of solvents or have no solvents at all.

This invention is applicable preferably to any "oil" and "hydrocarbon", wherein with these terms is meant to include the unrefined and refined hydrocarbonaceous products derived from petroleum or from liquefaction of coal, both of which contain sulfur compounds; these terms include, particularly for petroleum based 20 fuels, wellhead condensate as well crude oil which may be contained in storage facilities at the producing field and transported from those facilities by barges, pipelines, tankers, or trucks to refinery storage tanks, or, alternatively, may be transported directly from the producing facilities through pipelines to the refinery storage tanks; these terms also include refined products, interim and final, 25 produced in a refinery, including distillates such a gasolines, naphthas, gas oils, distillate fuels, oils, residues, residual fuels, fuel oils, and plant charges.

30 Asphaltenes flocculation is responsible of a number of operating problems during processing of petroleum products; examples of these are filter and burner plugging during fuel oil combustion, apparatuses fouling during crude oil extraction and processing .

All the examples hereinafter reported are to be intended for the mere purpose of illustration and should not be construed as limiting the invention.

Fuel oils are obtained by mixing heavy and light/medium distillates cuts from petroleum refining operations. Examples of heavy cuts are: atmospheric, vacuum and visbroken tars; examples of light/medium distillates cuts are: kerosene, 35 atmospheric, vacuum, visbreaker and catalytic cracker gas oils. Other cuts can be used for blending, depending on refinery lay-out and market situations. Fuel oils all contain however three groups of components: a) asphaltenes, which are heavy molecules with molecular weight (MW) even 50000; b) resins, which are polar molecules acting as "solubilizing" agents for asphaltenes in the hydrocarbon matrix; 40 c) oil phase or matrix, which is the major component. Resins and oil phase together form the so-called "malthenes"; asphaltenes and resins together form the so-called "micelles". Following to matrix chemical nature (asphaltenic, naphthenic, paraffinic), asphaltenes "solubility" is very different. In certain cases there is an effective incompatibility between different types of oils, which leads to 45 precipitation of part of the oil. This phenomenon is particularly felt since cracking stocks have been a part of fuel oil formulations; these fuel oil evolve during

storage, leading to a progressive viscosity increase, due to molecules rearrangement and asphaltenes precipitation. This, in turn, leads to several operational problems like, e.g., filter and burner plugging, deposit formation, etc. Such problems are solved by careful blending, by eliminating the asphaltenes fraction or by chemical additives.

Among the refinery plants designed to face the problems caused by asphaltenes, are solvent-deasphalting and hydroconversion. Solvent-deasphalting of hydrocarbon is carried out by mixing 2-4:1 of a solvent (pentane, eptane, methyl carbonate, etc.) to an hydrocarbon feed; solvent is recovered after asphaltenes separation.

Hydroconversion of heavy cut stocks by using Co-Mo catalyst is an already known process, in which catalyst amount is roughly 1-1000 ppmv (as metal) of the charge and hydrogen is normally in a ratio 100-10000:1 with charge, at a pressure of 500-3000 psig; catalyst precursors can also be used, which are hydrocarbon soluble metallic compounds that are converted in the active catalytic form during the process.

US 4,944,863 describes a process for treating heavy petroleum stocks, which comprises thermally hydrocracking the stock in the presence of a substantially inert solvent (e.g. 1-methylnaphthalene, toluene) and  $H_2$ , preferably under supercritical conditions. The process permits high conversion hydrocracking and  $H_2$  addition to be accomplished in the absence of catalyst or additives. EPA 419123 also refers to the same matter, specifying that the inert solvent ranges from 10 to 90% of the mixture, preferably 15-40%, the temperature from 370 to 510 °C, preferably 410-470 °C, and the pressure from 35 to 208 bar, preferably 70-139 bar, the solvent is in its supercritical or dense supercritical state and is not hydrogen donor, i.e., substantially inert under reaction conditions. The process facilitates  $H_2$  addition to the feedstock;  $H_2$  circulation is 90-1780  $Nm^3/m^3$  feedstock.

A number of processes have been developed to face the problem of asphaltenes stabilization.

US 4,428,824 describes a process in which a low-viscosity low pour-point petroleum product is produced by conventional visbreaking of a deasphalted residual petroleum feed followed by reblending of the recovered asphaltenes fraction.

EPA 102,763 describes a process in which sediment formation of unconverted petroleum residues remaining from a conversion process is reduced by blending with the unconverted residue 2-4 wt.% of a residue containing > 8% wt.% asphaltenes.

US 4,179,000 describes a process for reducing the S content of petroleum asphaltenes utilizing water, MeOH,  $CO_2$  and their mixtures in supercritical conditions. The ratio of the petroleum asphaltenes and the fluid is 1:0.3-1.3.

US 5,057,204 describes a process for visbreaking, improved by incorporating into the feedstock a catalyst preferably supported on a substrate; the catalyst is the elemental form or compound of an element selected from Se, Te and S.

Few chemicals are used to solve the problem; all of them are of the dispersant type like, e.g., phosphate esters; condensation product between: i) cyclic anhydride and alkylpolyamine, ii) ethossilated amine and carboxylic acid; sequenced copolymers.

Due to their structure, asphaltenes give rise to several operational problems in refinery processing apparatuses, e.g. fouling in furnaces and heat exchangers; moreover, they contribute to stabilize water in oil emulsions. The result of fouling appear in the form of heat transfer loss, pressure drop, loss in throughput rate and increase in corrosion of the equipment.

Coke and fouling deposition is generally experienced when hydrocarbon liquids and vapours contact the hot metal surfaces of petroleum processing equipment. It is thought that the hydrocarbons undergo various changes through either chemical reactions and/or the decomposition of various unstable components of the hydrocarbons. The undesired products of these changes in many instances include coke, polymerized products, deposited impurities and the like. The same phenomenon of coke and fouling deposition also occurs on catalysts. Fouling of catalysts causes a decrease in activity and/or an increase in reactor pressure drop, which leads to discharge the fouled catalyst from the reactor.

The charge stocks which most commonly cause fouling in refinery apparatuses are naphthas, gas oils, crude, residues and petroleum gases. Another class of hydrocarbons where fouling arise and which are ameliorated by present invention is the petroleum gases or normally gaseous alkane and alkene hydrocarbons which normally boil in the range of  $-250^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , i.e., methane, ethane, propane, butane, ethylene, propylene, etc. These hydrocarbons may be in the liquified state or gaseous state during processing thereof in the practice of the present invention.

The various charge stocks mentioned above are most frequently subjected to one or more of the following general type thermal or catalytic processes to produce fuel: fractionation, reforming, cracking, alkylation, isomerization, polymerization, desulfurization, hydrogenation and dehydrogenation.

Similar fouling problems arise in equipment used in petrochemical industry where the hydrocarbon charge stock is, in most cases, heated at normal or elevated temperatures and pressures. For example, acetylene may be produced from light naphtha or natural gas. Benzene and hydrogen are reacted to produce cyclohexane. Light alkane hydrocarbons may be used to produce olefins. Light and heavy crude oils, as well as light hydrocarbon gases may be cracked into ethylene, propylene and  $\text{C}_4$  olefins.

The foregoing examples of petrochemical processes are illustrations but not exhaustive of processes where fouling problems arise such that the practice of the present invention may be used advantageously.

The same mechanism of coke and fouling formation occurs during fuel combustion and will lead, e.g., to coke deposition in internal combustion engines and soot formation.

For many years there has been a search for engine additive that, when injected directly into the upper cylinder areas, would exert a profound cleaning effect and thus serve to remove carbonized varnishes and sludge deposits that form on spark plugs, fuel orifices, intake valves, fuel injectors and cylinder walls. These deposits inhibit the optimum burning of fuel and Km-per-liter efficiency is reduced. Additionally, such deposits promote the generation of unburned hydrocarbons and partially burned pyrolysis products during combustion of gasolines and diesel fuels: all of these compounds pose serious environmental hazards.

Particulate emissions during combustion of fuel oils is a serious environmental problem. They bear from unburned fuel droplets, as a core of heavy compounds is generated during combustion: the droplet start to combust at the outer, lighter part, leaving unburned the inner heavy part. The contribution to the coke particle from both asphaltene and maltene components is significant. Particulate emissions may be best reduced through enhanced particle burnout.

The previous state of the art directed toward atomization methods improvement, as good atomization will produce the fine droplet sizes needed for good vaporization which, in turn, produces good combustion, as the smallest droplets vaporize completely; but in the larger droplets formed from heavier fuels, which in turn have a high viscosity, liquid phase cracking occurs, which lead to the undesirable formation of carbonaceous residue, often in the form of a cenosphere.

It is well-known that fluid in supercritical conditions increase solids solubility. The utilization of supercritical fluids in industry is well documented. The application of supercritical extraction competes with technologies as liquid solvent extraction and distillation. In the field of natural materials are included supercritical fluid extraction of unwanted substances such as caffeine and nicotine and the separation of constituents such as food essences and drugs. For fossil fuels, application of supercritical fluid extraction include enhanced oil recovery, extraction of liquids from coal, and fractionation of heavy petroleum liquids. Supercritical fluid extraction utilized in synthetic fuels application include coal processing such as solvent coal extraction, coal liquefaction, extraction of carbonaceous residua, and an integrated process of producing methanol from coal followed by conversion to gasoline. These processes uses supercritical fluids such as normal paraffins, olefins, halogenated light hydrocarbons, carbon dioxide, ammonia, sulfur dioxide, toluene and other similar aromatics, bicyclic aromatic and naphthenic hydrocarbons, alcohols, aldehydes, ketones, esters and amines, and they are usually carried out above the critical temperature and pressure of the solvent. US Patents 3,558,468 , 4,192,731 , 4,251,346 , 4,376,693 , 4,388,171 , 4,402,821 , 4,443,321 , 4,447,310 , 4,508,597 and 4,675,101 are some examples which disclose processes wherein coal is contacted with one or more of the aforementioned solvents under supercritical conditions until significant portions are dissolved in the solvent, then easily removed from residual solid materials, usually by filtration, and then the filtrate is separated by distillation into a solvent fraction for recycle and a liquid fossil fuel, which may be used directly as a fuel or further refined to yield a variety of hydrocarbon products, including diesel and jet fuels. Which purpose of the art is primarily obtaining other useful fuels from coal. Petroleum applications include converting feedstocks such as atmospheric and vacuum-distillation residues to cat-cracker and lubricating-oil feedstocks using lower boiling paraffins in supercritical fluid extraction processes, like pentane deasphalting. The feedstock is treated to achieve asphaltene precipitation, not asphaltene stabilization as in present invention. In addition to the above, supercritical fluid injection has been tested for tertiary oil recovery from petroleum reservoirs. This method is particularly suitable for the use of relatively inexpensive carbon dioxide.

- What fouling prevention concerns, a great number of compositions are patented for the scope. U.S. 4,425,223 describes a 50:50 wt. mixture of dodecyl benzenesulfonic acid and isooctyl hydrogen phosphate to reduce fouling of heat exchangers.
- 5 US 4,619,756 describes compositions of thiophene ring-containing polycondensed aromatic-naphthenic compounds (with average molecular weight 200-1000) dosed at 0.0001-0.01 wt.% in the hydrocarbon stream to be processed.
- U.S. 4,744,798 describes benzophenone derivatives for use as gasoline detergents.
- 10 US 4,551,226 discloses use of N,N-di-C<sub>1-18</sub>-hydrocarbylhydroxylamine at 10-50 ppmv as antifoulant for heat exchangers.
- US 5,128,022 describes an antioxidant composition useful for fouling control in petrochemical processes, comprising a p-phenyldiamine compound and a C<sub>1</sub>-C<sub>6</sub> organic compound.
- 15 FR-Pat. Appl. N. 83 18495 discloses a process for preventing coke formation during thermal treatment of high asphaltene content hydrocarbons by using compounds of metals like V, Mo, Cr, W, Fe, Co, and Ni, dosed at 100-2500 ppmv, referred to metal, based on hydrocarbon feedstock. Ni compounds are deemed to be most effective. Effectiveness of metallic compounds is increased by adding 0.05-5 wt.% DMDS. EPA 333554 however shed some light to the sole effect of
- 20 DMDS, in that it increases conversion.
- EPA 396384 describes a hydrocracking process in which the feedstock is admixed with a thermally decomposable catalyst precursor and then with hydrogen under hydrocracking conditions. The preferred catalyst is Mo naphthenate.
- IT 1211977 describes an antifoulant composition containing a tertiary aliphatic amine as antioxidant.
- 25 Other examples of antifoulant compositions are described in EPA 269,332, U.S. 4,752,374, US 4,440,625, US 4,842,716,
- What combustion regards, JP 58 53,985 describes a mixture of surfactants, kerosine, lauryl alcohol and an aqueous solution containing Cu, Fe, Ni, Sn, Pb, and
- 30 Ba naphthenates mixed to a fuel oil to give a fuel with improved combustion properties.
- ES 2,021,179 describes a combustion improver additive containing a tertiary aliphatic or cyclic amine, aliphatic or cyclic organic nitro derivatives, industrial lubricant, aliphatic or cyclic organic solvent and optionally a pour point depressant and a neutralizing agent.
- 35 US 4,435,185 discloses that the combustion properties of liquid hydrocarbon furnace fuels are improved by the addition of dinitrotoluene and, optionally, of a metal acetylacetonate; in such a mixture can be also added about 6000 ppmv of each o-dichlorobenzene, DMF, toluene and butyl cellosolve.
- 40 US 5,116,390 describes a combustion catalyst which comprises naphthalene, toluene and benzyl alcohol.
- JP 01 26,696 describes a combustion improver for hydrocarbon fuels mainly containing anisole and cumene, dosed at 1-250 ppmv in the fuels.
- EPA 506069 discloses processes and apparatuses in which supercritical fluids are
- 45 used as viscosity reduction diluents for liquid fuels or waste materials which are then spray atomized into a combustion chamber. The fluid, usually CO<sub>2</sub>, is brought in supercritical state in a separate apparatus and then mixed with the fuel

in an amount ranging from 10 to 60 wt.% based upon the total weight of the liquid mixture.

Other examples of combustion improvers compositions are described in JP 61 02,795, JP 03 17,187.

5 What asphaltenes stabilization concerns, JP 58 69,294 describes a process to prevent sludge formation in fuel oil storage tanks by the addition of 20-500 ppmv of a dispersing agent comprising a mixture (25-75:75-25) of an olefin-maleic anhydride copolymer (av. MW 2000-6000) amine salt and an ampholytic surfactant (e.g. lecithin).

10 DE 3,626,102 describes a fuel additive containing a mixture of : a) a polar, aliphatic, O-containing hydrocarbon (MW 250-500), b) a C<sub>4</sub>-C<sub>12</sub> alcohol, c) a hydrophilic parting agent (e.g. glycol monoether), d) a single-ringed aromatic hydrocarbon and e) hydrocarbon-base mixture.

FR 2,585,032 describes a fuel oil which contains a dispersant to avoid aggregation of asphaltenes, selected from a group consisting of A) an imidazoline derivate containing a C<sub>7</sub>-C<sub>23</sub> hydrocarbon group, B) an hydrolysis product of A, C) a reaction product of C<sub>8</sub>-C<sub>22</sub> aliphatic acid and polyalkylenepolyamine containing 4-6 -NH<sub>2</sub> groups, D) an amine containing a C<sub>8</sub>-C<sub>22</sub> hydrocarbon group, E) a polyamine containing a C<sub>8</sub>-C<sub>22</sub> hydrocarbon group, F) an etheramine containing a long-chain hydrocarbon, G) a phosphate containing a long-chain hydrocarbon, H) a salt of G, I) a dithiophosphate, and J) a salt of I.

20 JP 62,209,194 discloses that sludge deposition of unrefined oils from coal, oil shale or tar sands can be prevented by addition of 1-2 wt.% of monovalent alcohol to the oils.

25 US 4,516,981 discloses a sludge dispersant for residual fuel oils, which comprises hexanol 25 wt.%, diethylene glycol methyl ether 15 wt.% and Triton X100 60 wt.%, applied at 1wt. part per 1000 wt. parts oil.

FR 2,633,935 discloses that asphaltene flocculation in unstable heavy fuel oils is prevented by mixing the oils with an intermediate deasphalting fraction containing 30 >20 wt.% of asphaltenes precipitated with heptane or such a fraction modified by maleic anhydride in the presence of an amine.

WO 91/13951 discloses that asphaltene sediment in blends of residual fuel oils is reduced by treating the residuum with an alkylaryl sulphonic acid at 200 °C or above before blending.

35 Other examples of fuel oil stabilizers are described in JP 63 00,386, EPA 263,706, US 4,663,062, CA 2,029,465, BE 904,044, US 4,441,890, JP 63 23,991, US 5,011,504, CA 1,142,114.

What diesel fuel fouling and particulate emissions regards, US 4,723,963 describes a middle distillate hydrocarbon fuel (bp 160-400°C) with an improved cetane number. The fuel contains >0.5% wt. of hydrocarbon compounds (e.g. alkylaromatics and/or hydroaromatics) which contain benzylic alcohols or ketone species.

US 5,055,112 discloses that soot emission of diesel fuels is reduced by adding 500-5000 ppmv of an 1,2-alkanediol.

45 WO 85/00827 discloses usage of polybutylene glycol dodecylphenyl ether 2-aminoethylcarbamate for injection nozzle deposit control in diesel engines.



EPA 188,042 discloses  $\text{RNMe}_2$  ( $\text{R} = \text{C}_{4-20}\text{-alkyl}$ ) as storage stabilizers for diesel fuels.

US 4,822,378 discloses a composition for inhibiting color deterioration of diesel fuel, comprising a tertiary amine having the formula  $\text{RRNC}_6\text{H}_{11}$  and a hydroxylamine  $\text{RRNOH}$ .

US 4,867,754 describes a process for inhibiting deterioration of distillate fuel oil which comprises adding a synergistic mixture of a phosphite and a tertiary amine in the ratio 1-100/1-50.

EPA 487255 describes a hydrocarbon fuel composition suitable for an internal combustion engine, which comprises a hydrocarbon fuel and as a cleaning agent for carbonaceous deposits a compound selected from 1-(3-aminopropyl)-2-pyrrolidinone, 1-(3-aminopropyl)imidazole, N-hydroxyethyl imidazolidinone, N-aminoethyl-imidazolidinone and 2-(2-aminoethylamino)ethanol. The fuel can be a gasoline and include a carrier in which the cleaning agent is first dispersed before blending with the fuel; the carrier can be a lubricating oil, a polyether or a polymer of a  $\text{C}_2$  to  $\text{C}_6$  monoolefin.

WO 91/07578 describes compositions for cleaning deposits on an internal combustion engine which comprises: i) a hydrazine or an aliphatic amine; and ii) a hydrocarbon or substituted hydrocarbon having a ring wherein at least one half the atoms composing the ring are carbon. Compositions also contain a minor amount of water and ammonium hydroxide.

Other examples of deposits inhibitor compositions in diesel fuels are described in JP 62 68,891, US 4,509,952,

For removing deposits in oil-field extraction equipments, US 4,379,490 discloses that asphaltene deposits are removed from oil and gas wells, oil-field equipment, flow lines by treatment with a dialkyl disulfide oil activated by the addition of 10 wt.%  $\text{Et}_2\text{NH}$ .

Other examples of deposits removing compositions are described in DE 3,511,760.

What catalyst fouling regards, EPA 351,186 describes a process for reducing catalyst bed fouling by adding to the feedstock an effective amount of a  $\text{C}_2\text{-C}_{24}$  alkylamine, optionally in combination with an alkylarylsulfonic acid. Dosage of the resulting antifoulant composition is 25-150 ppmv.

US 4,372,840 describes a method for reducing the amount of coke produced during the cracking of hydrocarbon feedstock. The method comprises adding a hydrogen donor to the reaction zone and adding an effective amount of a metal passivator.

Asphaltenes are by definition those components that precipitate by adding n-heptane.

Asphaltenes stability is believed to be determined by  $\pi\text{-}\pi$  interactions between polyconjugated aromatic systems of adjacent molecules, that associates in stacked layers.

In fuel oil specifications asphaltenes stability is expressed in terms of dry sludge content, that is measured by HFT (Hot Filtration Test), and evaluated with analytical methods like SMS 2696 and IP 375. As asphaltenes stability decrease with increasing temperature, such methods measure the total amount of solids that

is filtered at 100 °C after washing with n-eptane. Today's HFT specifications for fuel oils range from 0.1 to 0.15 %.

The stability of residue, and hence of asphaltenes, arising from thermal processes depends upon reaction (and hence conversion) severity : HFT can even

5 significantly increase due to a minimum conversion increase.  
In all the thermal processes aiming at the conversion of residues and other heavy feedstocks, the main problem to be faced is related to the polycondensation of high molecular weight molecules such as resins and asphaltenes. These side reactions provide low value by-products (pitches and coke), impairs the stability of the  
10 wanted fuels, induces many difficulties in the process design and operation and, consequently, has to be prevented or at least carefully controlled. As in thermal activation all reactions involve free radical mechanisms, one of the best way to repress the polycondensation steps is to use donor compounds and more especially hydrogen-donors to capture the implicated radicals proceeding from structural  
15 modifications of the heaviest compounds of the crude.

Another problem related to residue utilization in fuel oil formulations is the compatibility among it and the cutter stocks and the compatibility among different types of fuel oils. This problem arises, among the others, from the dilution of the peptizing agent in the oil phase. In any case no paraffinic cutters can be uses as  
20 they destabilize asphaltenes .

When a fuel oil shows unstability problems it is possible to correct such parameter by mixing cracking residue with aromatic compounds. This imply at least a decrease in value of the cutter (e.g. LCO, gas oil, low sulfur fuel oil, aromatics), with related huge costs, due to cutter quantities needed and related price  
25 differentials. It is important that any corrective action be taken before the components of fuel oil are added to cracking residue, as asphaltenes, once flocculated, can hardly be solubilized in the oil phase. For the same reasons it is also important the sequence of blending operations .

Moreover, fuel oil instability can show itself after a certain period of time. As a  
30 matter of fact, as the system asphaltenes/oil is a viscous media, phase changes happen in a slow way. HFT content can vary, and accordingly the stability, after long storage periods and/or due to heating; the variation being related to fuel oil nature.

An improvement of the state of the art would be realized by achieving an HFT  
35 correction by use of a chemical additive to be used in sparing quantities.

Another improvement of the state of the art would be realized by rendering fuel oils stable to blending with paraffinic cutters and/or with other fuel oils.

In today's state of the art no additive composition is utilized to resolubilize flocculated asphaltenes, particularly what HFT correction concerns.

40 Some additives are used for avoiding apparatuses fouling, following asphaltenes precipitation, in oil fields. Their field of application is therefore more "easy", as asphaltenes destabilized in a crude are much less than those in a residue. In any case, their effect in the connection of HFT reduction, to our knowledge, has never been neither proposed nor proven.

45 Another problem related to asphaltenes is fouling formation in petroleum/petrochemical plants, as asphaltenes, among the others, constitute the heavier part of plant charge and induce the formation of agglomerates that limit

heat exchange and/or plant operability. Other foulants can be of the polymeric type (e.g. arising from alkenes) and/or condensation products (e.g. phenanelone-indane).

5 The presence of heavy compounds in plant charge limit their conversion in light products.

The presence of heavy compounds is moreover source of particulate and/or soot emissions during combustion. As a matter of facts, they constitute the core on which fuel droplet "grows" and defines its dimension: the droplet will burn from the outer part through the inner part and after vapourization of light products will remain a nucleus of unburnt matter. Such process is valid for both engine and burner combustion.

Heavy and/or condensation products are responsible of coke formation on catalysts of petroleum/petrochemical plants, which, in turn, limits conversion of such plants.

15 In today's state of the art those problems are solved by making use of different chemicals, e.g. of the dispersant type for limiting fouling or asphaltenes deposition, combustion catalysts for reducing particulate emission.

A dispersant is composed with an "anchoring" polar group and a "blocking" alkyl group; the polar group generally contains etheroatoms like: oxygen, nitrogen, phosphor. Dispersants adsorbs themselves on asphaltenes surface; adsorbed molecule serves as a repulsive barrier among such particles, avoiding their agglomeration and hence their precipitation.

20 The dispersants formulations having industrial interest are mainly: polymetacrylates, polyisobutylene succinimides, polyisobutylene succinates. A polyisobutylene succinate is obtained by reaction between a substituted succinic anhydride with an olefin and a polyhydric alcohol: a high MW polyester is obtained. The last asphaltenes dispersants generation is formulated with a laurylacrylate/hydroxyethylmetacrylate copolymer and a substituted phenol/formaldehyde resin (with MW around 3000). It is supposed that they function by substituting themselves to the naturally occurring resins. Also for these classes of compounds there is no evidence for any effect in reducing HFT. Other formulations of asphaltenes dispersants are of the type: alkylarylsulfonates, alcanolamine-alkylarylsulfonates and alkylarylsulfonic acids; all of them act as surfactants and increase crude oil surface tension above the level where precipitation occurs.

35 Other general purpose dispersants are of the type: a) substituted amines, where the substituent is an hydrocarbon containing at least 8 carbon atoms; b) acylated compounds containing nitrogen and having a substituent with at least 10 aliphatic carbon atoms, such substituent being obtained by reaction of an acylant carboxylic acid with at least an amminic compound containing at least a group -NH-, said acylant agent being joined to said aminic compound by way of a imido, amido, amidine or acyloxyammonium bridge; c) nitrogen containing condensated compounds of a phenol, an aldehyde and an amminic compound, having at least a group -NH-; d) esters of a substituted carboxylic acid; e) hydrocarbyl substituted phenols; f) alcoxylated derivatives of an alcohol, a phenol or an amine. To our knowledge all these compounds have not been used in the connection of present invention.

In a preferred embodiment the present invention provides hydrocarbyl and additives compositions that allow asphaltenes stabilization and/or their reeptization.

Surprisingly we have seen that glycols and halogenated hydrocarbons, alone or eventually admixed with common dispersants, have a positive effect, even in sparing quantities, on reeptization of flocculated asphaltenes, and hence on HFT. At major reason such compounds have an effect in avoiding asphaltenes destabilization.

Differing from today's state of the art, we utilize new types of compounds; moreover, they permit reeptization of flocculated asphaltenes. To our knowledge, the utilization of such an additive has never been proposed neither in connection with fuel oil treatment, for achieving their stabilization and/or asphaltenes reeptization, nor for HFT control and nor in connection with crude oil treatment during extraction and subsequent processing.

The utilization of the additives of present invention must then be regarded as surprising and out of the state of the art.

According to that, the present invention provides a process and additives and hydrocarbyl compositions able of reeptizing flocculated asphaltenes and/or avoiding their destabilization.

Compositions under present invention have been tested on laboratory and plant scale, measuring their effect with SMS 2696.

#### Example 1

A fuel oil has been additivized with 2000 ppmv of various compositions according present invention:

Formula	HFT (wt%)
Blank	0.56
85% naphtha solvent 15% o-dichlorobenzene	0.21
70% naphtha solvent 15% methylglycol 15% o-dichlorobenzene	0.18
70% naphtha solvent 30% o-dichlorobenzene	0.2
70% naphtha solvent 5% o-dichlorobenzene 15% methylglycol 10% butylglycol	0.13
70% naphtha solvent 30% triethyleneglycol	0.23
Commercial phosphoric esters dispersant	0.38
Commercial alkylarylsulfonates dispersants	0.48

#### Example 2

A refinery produced a fuel oil with HFT= 0.49%. From refinery experience, fuel oils for in house usage gave rise to combustion problems with HFT as low as 0.15%. After positive lab tests, the refinery decided to run a plant test to solve the problem. A chemical was dosed at 2000 ppmv, while mixing the fuel oil tank. After treatment HFT was reduced to 0.12%. The chemical had the following composition: 70% naphtha solvent 5% o-dichlorobenzene 15% methylglycol 10% butylglycol. During combustion of treated fuel oil no problem was noted.

The refinery also run some lab tests to prove fuel oil stability during eventual dilution for viscosity correction. Untreated fuel oil was not stable to dilution: by adding 10% of JP8 or kerosine the resulting HFT was not filterable. Treated fuel

oil was stable to dilution: by adding 10% of kerosine the resulting HFT was 0.08%.

### Example 3

5 A refinery received a fuel oil with HFT= 0.59%. Such refinery has a bottle-neck in a particular boiler - a not properly designed one - that gave rise to combustion problems with normal used fuel oils. It was then decided to test the new technology for asphaltenes stabilization, after positive lab tests. The chemical had to be added during discharging of fuel oil from storage tank to a little tank. First plant test was particularly significative.

10 Due to operational reasons, the receiving tank foot had an unextractable fuel oil (low sulfur, paraffinic in nature) volume of 346 m<sup>3</sup>. It was known that the mixture with high sulfur, asphaltenic fuel oil was not possible. This evidence was also proved in laboratory by running HFT of the mixture of the two fuel oils: when the high sulfur fuel oil content was higher than 20% the mixture was not filterable.

15 Surprisingly, it was seen that the chemical had a positive effect even in this severe case: mixtures of the high sulfur fuel oil were possible in any proportion, and the resulting HFT was around 0.2%.

Plant test confirmed those results: a mixture of 72% high sulfur fuel oil + 28% paraffinic fuel oil was realized, and the chemical was added during discharging of the high sulfur fuel oil in the receiving tank, without mixing the receiving tank. At the end of the test, HFT was evaluated at various heights:

20 tank foot	0.24%
1 m from tank foot	0.18%
2 m from tank foot	0.16%
25 3 m from tank foot	0.10%
4 m from tank foot	0.06%

The result were surely positive, although it is evident that near tank foot, fuel oil is more unstable in comparison with the rest of the tank. Total chemical dosage was 1878 ppmv.

30 As confirmation of the successful test, in no refinery apparatus was noted any problem during combustion of treated fuel oil.

Fuel oil characteristics were as follows:

Property	High sulfur F.O.	Low sulfur F.O.	Mix 72%HS+28%LS
Viscosity @ 50 °C (°E)	47.2	63.7	51
Viscosity @ 50 °C (cSt)	355.8	483	385
Pour point (°C)	+1	+26	+7
Sulfur (%)	2.27	0.74	N.A.
Asphaltenes (%)	7.8	3.7	8.2
HFT (%)	0.59	0.2	Not filterable

Given the positive results the entire tank was treated. Chemical dosage was even optimized at 1400 ppmv, obtaining HFT in the range 0.12 % - 0.15%. A further out of spec shipment was also treated with 1200 ppmv chemical, reducing HFT from 0.58% to 0.1%. The chemical being used had the following composition: 70% naphtha solvent 5% o-dichlorobenzene 15% methylglycol 10% butylglycol.

Compositions under present invention enable to maintain in a colloidal form all asphaltenes molecules present in fuel oil; they have, moreover, the advantage to be utilized in a curative manner, i.e., after precipitation and not solely in a preventive manner.

5 It is evident that glycols and halogenated hydrocarbons are more effective than commercial dispersants in reducing HFT and/or stabilizing and/or reprecipitating asphaltenes. Among the glycols are to be preferred the low molecular weight ones (preferably up to 280), among halogenated hydrocarbons are to be preferred halogenated aromatics. Moreover, it seems there is a synergistic effect among  
10 halogenated aromatics and glycols.

For the purposes of present invention all glycols and/or their derivatives can be utilized, such glycols and/or their derivatives being not in a polymeric form, in the sense they are molecules of single compounds, also in an adduct form, and not molecules constituted by a chain where a single monomer is repeated; under  
15 present invention are to be considered as single glycols the following compounds: tetraethyleneglycol; mono- and di- ethers, mono- and di- esters, ether-esters and thioethers of single glycols.

While not wishing to be bound by theory, it is believed that the probable action mechanism of glycols and halogenated hydrocarbons, either as single compounds  
20 or as synergic association, seems to be the one in which the halogenated increase asphaltenes solubility and glycols, specially when the low MW ones, "penetrate" the asphaltenic structure thus contributing its suspension in the medium (by possessing polar groups, they can cause repulsion between single asphaltenic particles). By difference with the state of the art, it seems there is not a compound  
25 adsorbed over the asphaltenic particle, but a compound that promotes a solubility/stability increase.

In the same way, any low MW polar compound and any halogenated aromatic or solvent could be utilized for the scope.

Another possible mechanism (probably complementary to the previous) is that in  
30 which, as glycols and/or halogenated hydrocarbons are excellent resin solvents (both synthetic and natural), resins are dissolved and rendered available for a major number of asphaltenes following their "delocalization"; it is also possible that in such mechanism of resins dissolution-delocalization, glycols, and/or compounds under present invention, apart penetrating asphaltenic particles remain in solution  
35 with resins and increase repulsion among micelles.

Without being bound to any specific theory, the action of additives compositions could also be the one in which asphaltenes solubilization brings a minor asphaltenes concentration in fuel oil "solution" and this, in turn, brings a "dissociation" (delamination) of clusters rather than their association (dynamic model of  
40 asphaltenes molecules (Chem. Eng. Sc. Vol.47, 9-11, 1992)).

Moreover, as asphaltenes are bound together by hydrogen bonds and Van der Waals forces, -OH and/or polar groups penetrate the clusters and provoke their dissociation, from which follows a minor HFT.

In particular, well accepted mechanisms for explaining resins and asphaltenes  
45 interactions are substantially two: cosolvent and/or specific interactions. Cosolvent is to be attributed to a major polarity given from resins to the oil phase in which asphaltenes are dispersed; specific interactions resins-asphaltenes happen

by way of hydrogen bonds. The last mechanism is to be considered of primarily importance in the peptizing action of resins. From this also follows the action of glycols and/or other compounds with -OH groups, as these can form with asphaltene stronger hydrogen bonds than that asphaltene-asphaltene and/or interact on  $\pi$ - $\pi$  layers among polyconjugated aromatic systems of adjacent molecules: in both cases asphaltene association will not be favoured.

The same effect can be shown by basic groups (e.g. amines, carbazoles, benzopyrroles, benzothiazoles, cyclic amides, quinolines, benzoquinolines, benzocarbazoles, thioquinolines, indoles, indolothienophenes, carbazothienophenes, imidazoles, etc.) and/or acidic groups (e.g. carboxylic acids, naphthenic acids, esters, etc.) for both the mechanism described above (interactions with hydrogen bonds and/or Wan der Waal forces) and the fact that asphaltene have an "internal" acid-base equilibrium that favours their association.

According to present invention it is then utilizable any organic compound which contains etheroatoms with at least one unshared electron pair, such that they can preferably form hydrogen bonds with asphaltene and/or heavy compounds present in the system. Etheroatoms under present invention are preferably selected from the group: N, O, Cl, Br, F, I, S.

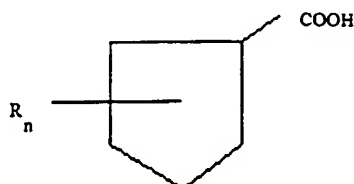
Among the compounds described above, are to be preferred those having hydroaromatics rings, as they favour hydrogen transfer and/or doning with coke and/or hydrocarbyl radicals formed during thermal degradation of a fluid under present invention.

Moreover, as it is known that changes in dielectric constant can determine changes in asphaltene colloids dispersion in petroleum residues, solvents having a different dielectric constant can increase asphaltene dispersion: their effect will probably depend from asphaltene's nature, in that different molecules will exert different "answers" to dielectric constant change. A list of solvents dielectric constants useful under present invention can be found, e.g., in the Handbook of Chemistry and Physics 74<sup>th</sup> Edition - CRC Press.

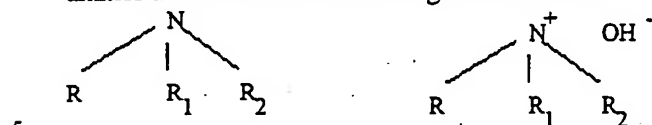
Other theoretical principles supporting present invention can be found hereinafter, e.g. concerning coal solubilization.

For the purposes of present invention can then be used the compounds selected from the following group: glycol of general formula  $\text{CH}_2\text{OH}-(\text{CH})_n\text{OH}_n-\text{CH}_2\text{OH}$  where  $n=0-10$ ; glycol ethers of general formula  $\text{R}_1-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{R}_2$  where  $\text{R}_1$  is an hydrocarbyl substituent  $\text{C}_1-\text{C}_{20}$  and  $\text{R}_2$  is H atom or an hydrocarbyl substituent  $\text{C}_1-\text{C}_{20}$ ; glycol esters of general formula  $\text{R}_1-\text{O}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{O}-\text{R}_2$  where  $\text{R}_1$  is an hydrocarbyl substituent  $\text{C}_1-\text{C}_{20}$  and  $\text{R}_2$  is H atom or an hydrocarbyl substituent  $\text{C}_1-\text{C}_{20}$ ; thioglycols of general formula  $\text{HO}-\text{R}_1-\text{S}-\text{R}_2-\text{OH}$  where  $\text{R}_1$  is an hydrocarbyl substituent  $\text{C}_1-\text{C}_{10}$  and  $\text{R}_2$  is H atom or an hydrocarbyl substituent  $\text{C}_1-\text{C}_{10}$ ; glycol ethers-esters of general formula  $\text{R}_1-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{O}-\text{R}_2$  where  $\text{R}_1$  and  $\text{R}_2$  are an hydrocarbyl substituent  $\text{C}_1-\text{C}_{20}$ ; halogenated hydrocarbons of general formula  $\text{R}-\text{X}_n$  where R is an hydrocarbyl substituent  $\text{C}_1-\text{C}_{20}$ , X is indifferently the atom Cl, F, Br, I and  $n=1-10$ .

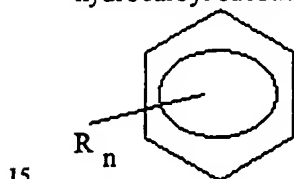
Other compounds according the present invention can be selected from the following group: naphthenic acids of general formula



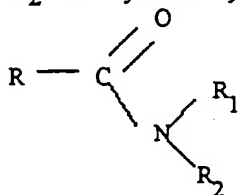
where R is an hydrocarbyle substituent  $C_1-C_{20}$  and  $n=0-4$ ; substituted esters of general formula  $R_1COOR_2$  where  $R_1$  or  $R_2$  is an hydrocarbyle substituent  $C_1-C_{20}$ ; amines and ammonium salts of general formula



where R and  $R_1$  are indifferently H atom, -OH group or an hydrocarbyle substituent  $C_1-C_{20}$ ,  $R_2$  the group -OH or an hydrocarbyle substituent  $C_1-C_{20}$ ; nitriles of general formula  $R-CN$  where R is an hydrocarbyle substituent  $C_1-C_{20}$ ; carboxylic acids of general formula  $RCOOH$  where R is an hydrocarbyle substituent  $C_1-C_{20}$ ; alcohols of general formula  $R-OH$  where R is an hydrocarbyle substituent  $C_1-C_{40}$ ; ethers of general formula  $R_1-O-R_2$  where  $R_1$  or  $R_2$  is an hydrocarbyle substituent  $C_1-C_{20}$ ; acetates of general formula  $CH_3COOR$  where R is an hydrocarbyle substituent  $C_1-C_{20}$ ; formates of general formula  $HCOOR$  where R is an hydrocarbyle substituent  $C_1-C_{20}$ ; substituted benzenes of general formula



where  $n=1-6$  and R can be indifferently H atom, -OH group, -COOH group, -CHO group, -NO<sub>2</sub> group, -NH<sub>2</sub> group, -SH group, -HSO<sub>3</sub> group, the same or different hydrocarbyle substituent  $C_1-C_{30}$ ; ketons of general formula  $R_1-CO-R_2$  where  $R_1$  or  $R_2$  is an hydrocarbyle substituent  $C_1-C_{20}$ ; sulfones of general formula  $R_1-SO_2-R_2$  where  $R_1$  or  $R_2$  is an hydrocarbyle substituent  $C_1-C_{20}$ ; sulfides of general formula  $R_1-S-R_2$  where  $R_1$  or  $R_2$  is an hydrocarbyle substituent  $C_1-C_{20}$ ; sulfoxides of general formula  $R_1-SO-R_2$  where  $R_1$  or  $R_2$  is an hydrocarbyle substituent  $C_1-C_{20}$ ; anhydrides of general formula  $R_1-CO-O-CO-R_2$ , included those where  $R_1$  and  $R_2$  are bound together to form cyclic anhydrides, where  $R_1$  or  $R_2$  is an hydrocarbyle substituent  $C_1-C_{20}$ ; amides of general formula



where R,  $R_1$ ,  $R_2$  are indifferently H atom or an hydrocarbyle substituent  $C_1-C_{20}$ ; thiolamines of general formula  $NR_1R_2SH$  where  $R_1$ ,  $R_2$  are indifferently H atom or an hydrocarbyle substituent  $C_1-C_{20}$ ; hetherocyclic compounds, preferably the hydrogenated ones, containing from 0 to 3 hydrocarbyle substituent  $C_1-C_{20}$ .



For the purposes of present invention heterocyclic compounds can be of different types, in that they contain atoms with free electronics pairs that, as seen above, contribute to both coke solubilization and to asphaltenes dispersion.

Heterocyclic compounds according present invention include preferably those selected from the following group: furans, thiophene, pyrrols, pirazoles, imidazoles, triazoles, dithiols, oxathiol, oxazoles, thiazoles, oxadiazoles, oxatriazoles, dioxazoles, oxathiazole, pyranes, pyrones, pyridine, pyridazine, pyrimidine, pyrazine, piperazine, piperidine, triazines, oxazines, oxathiazines, oxadiazines, morpholine, azepine, oxepin, thiepin, diazepine, indane, indenes, benzofuranes, benzothiophenes, indoles, pyrane-pyrrole, indazole, indoxazine, benzoxazole, anthranile, benzopyrane, coumarines, quinolines, benzopyrones, cinnoline, quinazoline, naphthyridine, pyrido-pyridine, benzoxazines, carbazole, xanthene, acrydine, purine, benzopyrroles, benzothiazoles, cyclic amides, benzoquinolines, benzocarbazoles, thioquinolines, indolothiophenes, carbazothiothiophenes, indoline, benzotriazoles.

By describing the previous group the compounds named in plural are to be intended as encompassing all the possible compound structures, including the iso-form : e.g. the term "dithiols" include 1,2 dithiol and 1,3 dithiol, "quinolines" include quinoline and isoquinoline.

As used in this specification the term "hydrocarbyl" refers to a group having a carbon atom directly attached to the rest of the molecule and having a hydrocarbon or predominantly hydrocarbon character. Among these, there may be mentioned hydrocarbon groups, including aliphatic, (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic, and aromatic-substituted aliphatic and alicyclic groups. Aliphatic groups are advantageously saturated. Examples include methyl, ethyl, propyl, butyl, isobutyl, pentyl, hexyl, octyl, decyl, octadecyl, cyclohexyl, and phenyl. These groups may, as indicated above, contain non-hydrocarbon substituents provided they do not alter the predominantly hydrocarbon character of the group. Examples include keto, halo, hydroxy, nitro, cyano, alkoxy and acyl. If the hydrocarbyl group is substituted, a single (mono) substituent is preferred. Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4- hydroxybutyl, 2-ketopropyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable heteroatoms include, for example, nitrogen, oxygen and sulfur.

Among the hereinabove compounds are to be preferred those selected preferably from the following group: trichloroethylene, tetrachloroethylene, methanol, ethanol, propanol, isopropanol, butanol, isobutanol, methylglycol monomethylether, butylglycol monobutylether, toluene, heavy amines (e.g. Solaria RS41, BP Chemicals), aryl sulfonates (e.g. Atlas MC 2343, ICI), glycerol, thioglycolic acid, naphthenic acid, o - dichlorobenzene, benzene, anthracene, carbon tetrachloride, carbon sulfide, pyridine, aniline, chloroform, tetraline, 1-methylnaphthalene, diphenyl, phenanthrene, o-cresol, phenol, nonylphenol, 1-methyl-2-pyrrolidinone, diethyl ether, dimethylformamide (DMF), tetrahydrofuran (THF), ethylenediamine, diethylamine, triethylamine, propylamine, 1-(3-aminopropyl)-2-pyrrolidone, 1-(3-aminopropyl) imidazole, N-hydroxyethyl-imidazolidinone, N-aminoethyl-imidazolidinone, 2-(2-aminoethylamino)ethanol,

furfurylamine, isopropylamine, cumene, 1,3,5 trimethylbenzene, 1,2,4 trimethylbenzene, indane, tetrahydroquinone, 4-hydroxyindane, ammonium octanate, maleic anhydride, tetrabutylammonium hydroxyde, thiophenol, p-toluidine, o-toluidine, thiophene, dipropylamine, quinoline, isoquinoline, 5 tetrahydroquinoline, diphenyl ether, hexamethylbenzene, propylbenzene, cyclohexylamine, 1-isopropyl-4-methylbenzene, 1,2,3,5 tetramethylbenzene, isoamyl acetate, carbonylhydrazide, hydroquinone, diethylhydroxylamine (DEHA), hexanol, tetrahydrothiophene, morpholine, nitrobenzene, o-xylene, m-xylene, p-xylene, 2-mercaptobenzothiazole, butylamine, methylamine, p-chlorothiophenol, 10 5,6 dihydro-4-methylpyrane, 2-methylfuran, benzothiophene, benzophenone, piperazine, piperidine, mesitylene, hexamine, succinic anhydride, decahydronaphthalene, ethylbenzene, 1,2 dimethylnaphthalene, 1,6 dimethylnaphthalene, p-cymene, ethyl ether, isopropyl ether, ethoxybenzene, phenyl ether, acetophenone, o-chlorotoluene, m-dichlorobenzene, monoethanolamine 15 (MEA), diethanolamine (DEA), triethanolamine (TEA), cis-decaline, trans-decaline, diethyleneglycol, triethyleneglycol, tetraethyleneglycol, dodecylbenzene, lauryl alcohol, myristyl alcohol, salicylic acid, 8-hydroxyquinoline, benzotriazole, tolyltriazole, thiodiglycol, salicylic aldehyde, p-toluensulphonic acid, dibutylphthalate, dinonylphthalate, methylethylketone (MEK), 20 methylisobutylketone (MIBK), methyl-tert-butyl-ether (MTBE), sulfolane, cyclohexane, 3,6-dioxyphtalimide, 3,6-tetramethyldiaminoxantone,  $\alpha$  naphthylamine,  $\beta$  naphthylamine, acrydine, fluorescein, coumaric acid, 1-naphthol-4-sulphonic acid, 2-naphthol-3,6-disulphonic acid, naphthothionic acid,  $\beta$  naphthol,  $\alpha$ -naphtholsulphonic acid, 1,4-naphtholsulphonic acid, coumarine, mixtures 25 methanol/KOH, 2-aminoethanethiol, dimethylaminothiol, diethylaminothiol. To all these compounds are to be added the following compounds, hereinafter better defined: BDM, GCAG, GSAG, by-products and/or waste products of industrial activities.

Some of these compounds are known as asphaltene stabilizers, e.g. alkylphenols, 30 but they have never been utilized for reducing HFT and/or in other connections of the present invention.

#### Example 4

It was added 10% of CFO (Cracking Fuel Oil- from Ethylene plant) to a fuel oil, the mixture being not filterable. HFT resulted 0.11% by adding 4000 ppmv of the 35 following additive composition: 85% naphtha solvent 15% commercial naphthenic acid.

Additives according to present invention differentiate with the state of the art in that: a) are not composed of polymeric, copolymeric and/or long chain compounds, but of single "monomers"; b) probably they do not adsorb on surface 40 particles, but they penetrate them; c) they contribute to increase asphaltene solubility in oil phase; d) are composed preferably with low MW compounds; e) they do not act exclusively by repulsive action between asphaltene particles; f) can "delocalize" resins.

For example, nitrobenzene has a strong effect on asphaltene MW, while pyridine 45 removes mostly of occluded resins.

The examples hereinabove reported confirm that additives under present invention act as a reeptizer for precipitated asphaltenes and prevent them, even in difficult conditions, from destabilizing. If such additives compositions act in such a way, at better reason they will positively perform in "easier" situations, like asphaltenes stabilization in a crude oil.

In another preferred embodiment the present invention provides a process, additives and crude oil compositions capable of reducing and/or preventing fouling during crude oil production.

During crude oil production, asphaltenes flocculation e their subsequent precipitation originates from the many occurring chemical, electrical and mechanical processes, included: a) addition of low surface tension liquids; b) asphaltenes particles oxydation; c) low MW gases release; d) acid washings; e) electric charge neutralization during fluid flow.

The various thermal, mechanical and solvent methods normally utilized for controlling paraffins are only partially effective in controlling asphaltenes deposition. This reduces the effectiveness of hot oil method and mechanical cleaning. Deposit remotion with solvent is only limited to aromatic fractions; moreover, pure aromatic solvents like xylene and toluene exert little or no effect in removing asphaltenic deposits of formations.

Additives compositions under present invention can find application in crude oil extracting processes (likewise in its refining processes) for being utilized, e.g. : a) emulsion breakers assistants; b) controllers of oil/water interface (asphaltenes set at such interface, thus stabilizing emulsions); c) sludge cleaners (e.g. in tank cleaning); d) well cleaners (both during production and injection); e) injection systems and water clarification assistants; f) jet pump and orifice cleaners; g) apparatuses cleaners (e.g. heat exchangers, lines, columns, separators, etc.). Moreover, asphaltenes decrease (also referred only to their dimensions) brings a minor foaming.

#### Example 5

Asphaltenes dispersion tests have been performed with the following procedure: in 100 ml n-eptane was added roughly 1 g sample and then agitated for 1 minute; the mixture was allowed to stand for 10 minutes and then 50 ml of the liquid where pipetted for adding 50 ml n-eptane; solids amount (precipitated asphaltenes) was then noted. By using a fuel oil with HFT=0.56% and performing such test, in the blank as much as 33% of asphaltenese were precipitated, while in the fuel oil with 2000 ppmv of an additive (70% naphtha solvent 15% methylglycol 10% butylglycol 5% o-dichlorobenzene) only 4% of asphaltenes were precipitated. A commercial dispersant based on phosphoric esters gave no results.

#### Example 6

In a dispersion test, performed as in Example 5, a crude oil gave a 7% deposit. The same crude oil additivized with 1000 ppmv of a commercial dispersant based on alkylarylsulphonates gave a 6% deposit, while the addition of an additive under present invention (85% GCAG 15% MTBE) gave a 2% deposit; with another additive under present invention (85% methanol 15% tetrahydroxy-p-benzoquinone) the deposit was 3%.

In another preferred embodiment the present invention provides additives and hydrocarbon compositions exerting a minor fouling formation in petroleum/petrochemical plants.

5 In petroleum processes, infact, asphaltenes precipitation is one of the most important causes of apparatuses fouling. For example, preheat trains and heaters are subject to asphaltenes fouling, likewise columns, demister pads, included pumparound nozzles.

10 In a further preferred embodiment the present invention provides additives and hydrocarbon compositions exerting a minor fouling formation in process apparatuses and/or catalysts in the petroleum/petrochemical industry.

The term "coke" as used in present invention refers to the whole of non-distillable heavy solid compound and/or the heavier fractions of a hydrocarbon and/or fuel composition, generated in chemical and/or petrochemical and/or petroleum refining and/or metallurgical plants and/or oil field and/or engines and/or  
15 boilers and/or burners and/or furnaces of any kind, following, but not limited to, a thermal action upon a charge stream.

Fouling and coke generally show when hydrocarbons contact a heated metallic surface; changes happen then in their structure, via chemical reactions and/or decomposition of unstable components. Undesiderable products of said changes  
20 include coke, polymerized product and the like. The same phenomenon also occurs in catalysts.

During the process a small part of the oil undergo undesired side reaction which go through polymerizations and condensations to form solid substances that are deposited on the catalyst surface. The solid materials, which are of varying and  
25 often rather ill-defined structures, are collected under the generic term "coke". Coke causes loss of catalytic activity, through chemical interaction with the catalytic materials or through blocking of the access to the active sites. This deactivation reduces the lifetime of the catalyst and causes serious economic problems in the industry.

30 The present invention provides a method for increasing the time that a catalyst can be employed effectively without having to interrupt the process. The present invention also provides a process which will inhibit and/or suppress fouling of the catalyst bed. Surprisingly, the present invention is also useful for reversing the flow restricting effects of deposits already existing on a previously used catalyst.  
35 The present invention also provides a method of reducing the fouling of the catalyst bed by deposits without adversely affecting the catalytic properties of the catalyst to any significant degree.

In process apparatuses, when coke and/or fouling formation exceed acceptable limits (as monitored by e.g. skin temperature, fouling factor,  $\Delta P$ , etc.), the apparatus  
40 cannot be maintained on stream and must be cleaned.

Surprisingly, compositions under present invention can significantly reduce coke and/or fouling formation. When this reduction is driven a high levels an increase in distillation yields is also possible.

45 It is known that coal can be solubilized by utilizing chemical compounds that are able to extract coal contained hydrocarbons. Such compounds are used at a ratio of 2-3:1 with coal.

Non specific solvents are believed to extract, at temperatures  $< 100^{\circ}\text{C}$ , resins and waxes present in the coal matrix, although extract yield are low. Solvents as ethanol, benzene, acetone are in this class. Specific solvents dissolve 20-40% of the coal substance at temperatures  $< 200^{\circ}\text{C}$ . Nitrogen and oxygen compounds are generally good solvents due to the presence of an unshared electron pair, which makes the solvent polar (Fuel, 1951, 30, 145-148). Nitrogen compounds are generally better solvents than the oxygen ones. Extract yields as high as 35-40% can be obtained by extraction with pyridine, certain hetherocyclic bases and primary aliphatic amines; secondary and tertiary aliphatic amines are less effective because more than an alkyl group on the amine presents steric hindrance to interaction between the solvent and coal. Degrading solvents are effective when used at temperatures in the range of  $200-400^{\circ}\text{C}$ . Their action depends on the thermal degradation of the coal to form smaller and more soluble fragments. Phenanthrene, diphenyl and tar oil fractions are examples of this class. Reactive solvents dissolve coal by reacting with it at temperatures around  $400^{\circ}\text{C}$ . Examples of these solvents are compounds containing hydroaromatic rings: e.g. tetralin give higher coal conversion than their aromatic analogue and the hydroaromatic member of a hetherocyclic pair (such as indoline) is more effective than the aromatic member (indole). These solvents can act as hydrogen donor or as hydrogen transfer agents. Cycloalkanes behave the same either alone or as a part of a solvent mixture. When used with polyaromatic compounds having 3 or more rings as solvents, cyclohexanes donate hydrogen in the presence of coal-derived radicals, giving rise to high extraction yields. Isopropyl alcohol and methyl alcohol can act as hydrogen donors to coal; the transfer of the hydrogen by the alcohol can be promoted by the presence of either potassium isopropoxide or KOH (Fuel, 1979, 58(6), 433-437). Other solvents useful in coal solubilization are selected from the group: phenol and p-toluene sulphonic acid (used as catalyst), cresol, formamide, acetonitrile, nitromethane, acetic acid, dioxane, tetrahydrofuran, diethyl ether, dimethylsulphoxide, dimethylformamide, ehtylenediamine, 1-methyl-2-pyrrolidinone, methylethylketone, 1,2 dimethoxyethane. A particular application of these compounds is supercritical coal extraction; as a matter of fact, it is known that fluids in supercritical condition increase solid solubility.

Neither utilization of such compounds nor the utilization of supercritical fluids has never been proposed in connection with petroleum/petrochemical industry (apart tetralin and/or dimethylsulphoxide at dosages 3-5% referred on charge and not in supercritical condition), specially concerning fouling and/or coke reduction or, much less, for increasing distillation yields. Their utilization in such connection must be regarded as novelty in the state of the art.

As a matter of fact, if those compounds are able to solubilize coal, at better reason they will solubilize the heavy crude oil components and/or coke formed in the apparatuses, which in turn means less coke/fouling/HFT and/or more yields. Particularly, the amount of additive injected will be more than coke present and/or deposited on apparatuses, thus achieving its solubilization. Without interpreting it as a limitation of present invention, some of those compounds, useful in coal solubilization, have been cited hereinabove.

Performance are enhanced when the compound of choice will be in supercritical state at the "normal" process conditions in the plant where it is added. In such connection, it is believed that the compound of choice will be more effective by having a lower critical pressure and a critical temperature approaching that of the process, with respect to the process where it will be applied. For example, for a thermal processes the range will be 480-500 °C and 1,4-3 MPa. The compounds of choice will be preferably selected among those that exert an improvement in asphaltene stabilization.

This constitutes an important difference with the state of the art of supercritical fluid applications in that, in coal extraction or during combustion, these compounds are artificially brought in supercritical state in specifically designed plants: in the process under present invention compounds are specifically chosen in a way they are, preferably, in supercritical state, or dense supercritical state, at normal operating conditions of existing plants. In particular, there is no petroleum/petrochemical plant that uses an "external" fluid (i.e. a fluid not designed for that plant) which becomes supercritical upon entering the process, and which has an influence on yield/coke/fouling.

Supercritical gas extraction is analogous to both solvent extraction and distillation. Whereas leaching of a solid by a stream of liquid is a form of liquid extraction, vaporization of a substance into a stream of carrier gas is a form of distillation. However, below its critical temperature, the solvent will be liquid, while above its critical temperature it will be gaseous whatever the pressure. Thus both processes can be realized with the same solvent. In supercritical extraction the carrier gas is a supercritical gas and under the conditions which are realized it is difficult to distinguish physically between the two processes.

Slight changes in the temperature and pressure in the critical region cause extremely large changes in the solvent density and thus its dissolving power. Density, viscosity and diffusivity for typical supercritical fluids are intermediate between those of a liquid and a gas. Although a supercritical fluid has a density approaching that of a liquid for high solvent capacity, the diffusivity is orders of magnitude greater giving improved mass-transfer rates.

In supercritical gas extraction under present invention, an organic solvent under supercritical conditions is used for the extraction of extractable substances. The process involves the selective extraction of hydrogen rich compounds of extractable substances and is based on the ability of a heavy substance to vaporize in the presence of a compressed supercritical gas. For example, the products obtained upon heating coke to 400 °C cannot be separated by distillation from the parent coke because of the low temperature, whilst at higher temperatures polymerization of the products takes place, which is undesirable; however, when compressed solvent vapors are used near their critical temperature the heavy organic coke components acquire a high volatility. Under favourable conditions an increase of 1000 times in volatility can be achieved which permits the extraction of low volatile compounds at temperatures considerably lower than their boiling points.

Being in a supercritical state is an improved condition for performance, but not limitative: as a matter of fact, as obvious from this specification, under present invention there are a number of additive compositions capable of reducing

fouling/coke at atmospheric pressure. Obviously, such compositions will be more effective when their components will be in a supercritical state under normal operating plant conditions.

Among the compounds showing effectiveness in coke reduction are to be preferred those selected from the following group: trichloroethylene, tetrachloroethylene, methanol, ethanol, propanol, isopropanol, butanol, isobutanol, methylglycol monomethylether, butylglycol monobutylether, toluene, heavy amines (e.g. Solaria RS41, BP Chemicals), aryl sulfonates (e.g. Atlas MC 2343, ICI), glycerol, thioglycolic acid, naphthenic acid, o - dichlorobenzene, benzene, anthracene, carbon tetrachloride, carbon sulfide, pyridine, aniline, chloroform, tetraline, 1-methylnaphthalene, diphenyl, phenanthrene, o-cresol, phenol, nonylphenol, 1-methyl-2-pyrrolidinone, diethyl ether, dimethylformamide (DMF), tetrahydrofuran (THF), ethylenediamine, diethylamine, triethylamine, propylamine, 1-(3-aminopropyl)-2-pyrrolidone, 1-(3-aminopropyl) imidazole, N-hydroxyethyl-imidazolidinone, N-aminoethyl-imidazolidinone, 2-(2-aminoethylamino)ethanol, furfurylamine, isopropylamine, cumene, 1,3,5 trimethylbenzene, 1,2,4 trimethylbenzene, indane, tetrahydroquinone, 4-hydroxyindane, ammonium octanate, maleic anhydride, tetrabutylammonium hydroxyde, thiophenol, p-toluidine, o-toluidine, thiophene, dipropylamine, quinoline, isoquinoline, tetrahydroquinoline, diphenyl ether, hexamethylbenzene, propylbenzene, cyclohexylamine, 1-isopropyl-4-methyl-benzene, 1,2,3,5 tetramethylbenzene, isoamyl acetate, carbonylhydrazide, hydroquinone, diethylhydroxylamine (DEHA), hexanol, tetrahydrothiophene, morpholine, nitrobenzene, o-xylene, m-xylene, p-xylene, 2-mercaptobenzothiazole, butylamine, methylamine, p-chlorothiophenol, 5,6 dihydro-4-methylpyrane, 2-methylfuran, benzothiophene, benzophenone, piperazine, piperidine, mesitylene, hexamine, succinic anhydride, decahydronaphthalene, ethylbenzene, 1,2 dimethylnaphthalene, 1,6 dimethylnaphthalene, p-cymene, ethyl ether, isopropyl ether, ethoxybenzene, phenyl ether, acetophenone, o-chlorotoluene, m-dichlorobenzene, monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), cis-decaline, trans-decaline, diethyleneglycol, triethyleneglycol, tetraethyleneglycol, dodecylbenzene, lauryl alcohol, myristyl alcohol, salicylic acid, 8-hydroxyquinoline, benzotriazole, tolyltriazole, thiodiglycol, salicylic aldehyde, p-toluensulphonic acid, dibutylphthalate, dinonylphthalate, methylethylketone (MEK), methylisobutylketone (MIBK), methyl-tert-butyl-ether (MTBE), sulfolane, cyclohexane, 3,6-dioxyphtalimide, 3,6-tetramethyldiaminoxantone,  $\alpha$  naphthylamine,  $\beta$  naphthylamine, acridine, fluorescein, coumaric acid, 1-naphthol-4-sulphonic acid, 2-naphthol-3,6-disulphonic acid, naphthothionic acid,  $\beta$  naphthol,  $\alpha$ -naphtholsulphonic acid, 1,4-naphtholsulphonic acid, coumarine, mixtures methanol/KOH, 2-aminoethanethiol, dimethylaminethiol, diethylaminethiol. To all these compound are to be added the following compounds, hereinafter better defined: BDM, GCAG, GSAG, by-products and/or waste products of industrial activities.

As said before, it is better to select compounds with a lower critical pressure and a similar critical temperature with respect to the processes where the additives under present invention are used. In petroleum processes, e.g., operating pressures

vary between 0.1-8 MPa, depending on the plant under consideration. Generally speaking, the higher pressure are reached in catalytic reactors (e.g. Reforming, Hydroconversion); inside heaters the pressure can vary between 0.4-3,5 MPa; inside heat exchangers the pressure can vary between 0.4-3,5 MPa;

- 5 A list of compounds that can become supercritical under present invention can be found, e.g., in the Handbook of Chemistry and Physics 74<sup>th</sup> Edition -CRC Press- pages 6-54 through 6-65. Among these are to be preferred those selected from the following group: tetrachloromethane, dimethylamine, ethylamine, ethyl formate, methyl acetate, dimethylformamide, propanol, propylamine, 10 isopropylamine, trimethylamine, tetrahydrofuran, ethyl vinyl ether, ethyl acetate, propyl formate, butanol, methyl propanol, diethyl ether, methyl propyl ether, isopropyl methyl ether, diethyl sulfide, butylamine, isobutylamines, diethylamine, cyclopentanol, pentanones, 2-methyltetrahydrofuran, tetrahydropyran, pentanal, butanoic acids, isobutyl formate, propyl acetate, pentanoic acid, butyl methyl ether, 15 tert-butyl methyl ether, ethyl propyl ether, bromobenzene, chlorobenzene, aniline, methylpyridines, cyclohexanone, cyclohexane, methylcyclopentane, cyclohexanol, hexanal, pentyl formate, isobutyl acetate, 2-ethoxyethyl acetate, methyl pentyl ether, dipropyl ether, diisopropyl ether, hexanol, methyl pentanols, triethylamine, dipropylamine, diisopropylamine, benzonitrile, benzaldehyde, toluene, cresols, 20 benzyl alcohol, methylanilines, dimethylpyridines, furfural, pyridine, methylcyclohexane, heptanol, acetophenone, ethylbenzene, xylenes, ethylphenols, xyenols, anilines, heptanol, acetophenone, ethylbenzene, xylenes, ethylphenols, xyenols, dimethylaniline, ethylaniline, octanenitrile, ethyl propanoate, methyl butanoate, methyl isobutanoate, propyl propanoate, ethyl 2-methyl propanoate, 25 methyl pentanoate, heptanoic acid, octanoic acid, 2 ethylhexanoic acid, propyl 3-methylbutanoate, octanoles, 4-methyl-3-heptanol, 5-methyl-3-heptanol, 2-ethyl-1-hexanol, dibutyl ether, di-tert-butyl ether, dibutylamine, diisobutylamine, quinoline, isoquinoline, indan, cumene, propylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, mesitylene, o-toluidine, N,N-dimethyl-o-toluidine, nonanoic acid, nonanols, naphthalene, butylbenzene, isobutylbenzene, cymenes, p-diethylbenzene, 1,2,4,5-tetramethylbenzene, decahydronaphthalene, decanoic acid, 30 decanol, 1-methylnaphthalene, carbazole, diphenyl, hexamethylbenzene, dodecanols, diphenyl methane, tridecanols, tetradecanols, hexadecanols, heptadecanols, terphenyls, octadecanols, eicosanols.
- 35 The compounds named with a plural refer to all possible isomer of the compound: e.g. the term "xylenes" refer to o-xylene, m-xylene and p-xylene.

Of particular interest are those compounds having a critical pressure ( $P_c$ ) < 5 MPa, preferably those with a  $P_c$  < 3.5 MPa.

A list of compounds with their relative critical constants is reported hereinafter:

Compound	Critical temperature (°C)	Critical pressure (bar)
p-Toluidine	394	23
Ethyl butyrate	293	30
Dipropylamine	277	31
Isobutyl acetate	288	31
Propyl acetate	276.2	32.9
Propyl-ethyl-ether	227.4	32.1



Triethylamine	262	30
Ethylbenzene	344	38
Propylbenzene	365,2	32,3
Butylbenzene	387,2	30,4
Cumene	357,9	32,3
para-xylene	342,8	36,1
Hexamethylbenzene	494	23,5
Triethanolamine	514,3	24,2
Diphenyl methane	497	28,6
Diphenyl	516	38,5
MTBE	224	34,3

A particular note is to be made for Solaria RS 41: as it is known that  $P_c$  decreases with increasing aliphatic chain length, and Solaria RS 41 is a heavy amines mixture, it will probably have a low  $P_c$  and will be effectively used in such connection. The same for all the other commercial heavy amines mixtures.

5 Other compounds cited hereinabove are of utmost importance for the purposes of present invention. For example, 1-tetradecanol has a  $T_c=474^\circ\text{C}$  and a  $P_c=1.81\text{ MPa}$ , with a  $bp=289^\circ\text{C}$ : at the operating conditions of a Coking Unit it will be in the supercritical state and will solubilize the coke formed in the furnace (the pressure inside furnace tubes is  $> 2.5\text{ MPa}$  and the temperature  $> 480^\circ\text{C}$ ). The same for hexamethylbenzene.

10 For Visbreaking, operating conditions range from a temperature of  $420-500^\circ\text{C}$  and pressure inside furnace tubes  $< 2.5\text{ MPa}$ . At operating conditions a liquid phase cracking occurs. Generally, Visbreaking severity is referred to as light products yield, that is gases and gasoline, absolute or at isoviscosity. Maximum admitted severity is determined by residue stability, which differs depending on charge.

15 Following Visbreaking reactions, a slow kinetic asphaltene flocculation can occur, with consequent residue and related products instability (bitumes, fuel oils), which leads to sludge formation.

For reducing HFT and/or CCR and/or for increasing yields, under present invention it is also possible to utilize all those solvents, and their mixtures, used for coal solubilization: this is valid for what is reported for industrial applications and for laboratories studies. Without regarding it as a limitation of present invention, some of these compounds have been already reported in this specification.

20 To evaluate effectiveness of additive compositions under present invention it was also used the test ASTM D-4530, where the sample is heated, with a temperature program, up to  $500^\circ\text{C}$  in a nitrogen atmosphere; this temperature is hold for 15 minutes and then the sample is allowed to cool: sample weight before and after thermal treatment gives the Conradson Carbon Residue or CCR.

25 Overall the specification and claims, the term "CCR" includes the Conradson Carbon Residue or the Ramsbottom Carbon Residue or any method for determining the carbon residue of a hydrocarbon.

30 A specific mention is to be made for the solvent utilized in additives formulations.

35 Normally, additives utilized in the hydrocarbon petroleum industry, but not limited to this, are diluted in a solvent, which main characteristic must be economicity,

apart non toxicity. For this purpose it is a common practice to utilize as solvent heavy aromatic naphthas (either the petroleum or the coal ones).

In an another preferred embodiment, present invention provides new solvents types for formulations of additive chemicals in the industry.

5 It is known that transesterification reaction between a vegetable oil and an alcohol (e.g. methanol, ethanol) leads to ester mixtures to be utilized as vegetable diesel fuel (biodiesel). In such a reaction glycerol is obtained as a by-product. Such glycerol is not pure, but contains non reacted fatty acids, alcohol and water. Typical composition of such by-product is, e.g., the following : 60-70% glycerol,  
10 15-30% fatty acids, 10-20% alcohol, 5-10% water. For further industrial utilization, this by-product is to be purified from fatty acids, alcohol and water and must be decoloured, which all leads to cost increases.

Surprisingly, we have seen that both ester mixtures (biodiesel), glycerol with  
15 and/or without fatty acids can be utilized as solvents for formulations of additive chemicals in the industry.

Preferably, in the hydrocarbon petroleum industry, corrosion inhibitors, neutralizers, antifoulant, antifoamers, antioxydants, sludge inhibitors, pour point depressants, CFPP depressants, emulsion breakers formulations and the like can be prepared with such solvents.

20 To these solvents can be effectively added compounds with "supercritical" properties or any other compound, and mixtures thereof, under the present invention.

Other types of glycerol derived as a by-product from chemical industry are useful for the present invention. Examples of these are, but not limited to, the following:  
25 glycerol aqueous solutions from the production of soaps and/or fatty acids; glycerol solutions from distillation of vegetable fatty acids; glycerol solutions from distillation of hydrolized fatty acids; glycerol solutions from distillation of hydrogenated fatty acids.

Moreover, as fatty acids can restore the acid-base equilibrium of asphaltenes, thus  
30 contributing to their stabilization, it is also useful to utilize fatty acids sources, competitive in terms of costs. Examples of these are, but not limited to, the vegetable acid oils not utilizable for human feeding and, in general, any kind of acid oil being a by-product of any production and/or a waste product.

All the oils, glycerols and by products defined as above can be utilized as new type  
35 of solvents under the present invention.

Throughout this specification the term "GCAG" refers to crude glycerol with fatty acids deriving from the transesterification reaction cited above, "GSAG" refers to glycerol without fatty acids (still containing alcohol and water and <4% of fatty acids) deriving from the purification of GCAG, and BDM refers to the mixture of  
40 esters deriving from the transesterification reaction cited above (biodiesel).

All these new types of solvents as defined above, are particularly effective in asphaltenes stabilization and in coke reduction, under present invention, and therefore are included in all the selected groups hereinabove. Their activity is also due to the presence of compounds under present invention (e.g. fatty acids, esters,  
45 alcohols, etc.).

Generally speaking, any by-product and/or any waste product deriving from any process, already known or to be implemented, that contains any compound, and

mixture thereof, under the present invention is to be regarded as encompassed by this invention.

#### Example 7

- 5 Tests with ASTM D-4530 were performed on a Visbreaker charge, constituted by a Vacuum residue, which charge was 80% Es-Sider 20% Brega. The results achieved by adding 1000 ppmv of additive formulations are listed below.

Formula	CCR
Blank	19.75
13155 (85% GCAG, 10% Toluene, 5% DMF)	16.56
13212 (85% GCAG 15% p-phenyldiamine)	17,34
13135 (85% BDM 15% MIBK)	16,98
13201 (85% GCAG 15% TEA)	17,42

In the additive compositions under present invention can be used other compounds, among those claimed, which posses particular properties.

- 10 For example, salicylic acid chelates iron and prevent the formation of Fe-asphaltenes aggregates, which is useful in antifoulant formulations.

Thiolamines cleave di- and polysulphide bridges present in heavy molecules, rendering thus possible achieving a minor sulfur content in fuel oil and/or coke (e.g. in Coking plants).

- 15 1-methylnaphthalene is reported to increase colloidal stability of paraffinic residues. Tetrahydroquinoline (THQ) is a powerful H-donor (>> tetraline) and can be utilized in such connection. Mixtures THQ-ethanol and THQ-tetraline (preferably with 2-10% THQ) can also be utilized.

4-hydroxyindane has a "combined solvent index" superior to THQ.

#### Example 8

- 20 A fuel oil has been additivized for CCR reduction with 1000 ppmv of the following additive compositions:

Formula	CCR
Blank	17,45
13080 (70% naphtha 15% toluene 15% xylens)	15,73
13126 (85% GCAG 15% naphthenic acid)	15,19

For evaluating additives performance in terms of yields increase we used simulated distillation test (ASTM D-2887) and/or thermogravimetric analysis and/or pilot plant studies.

- 25 Example 9

A Vacuum residue (80% Es-Sider 20% Brega) was additivized with 1000 ppmv of formula 13155 (85% GCAG, 10% Toluene, 5% DMF). The simulated distillation (ASTM D-2887) test was performed on this charge; the result are reported in figure 1.

- 30 A Vacuum residue (45% Lagotrec 55% Sarir) was additivized with 1000 ppmv of formula 13221 (85% GCAG 15% THF) and then charged to a Delayed Coking pilot plant with the following results:

Parameter	Vacuum Residue	VR+1000 ppmv 13221
H <sub>2</sub> S (wt%)	0.78	1.02
H <sub>2</sub> (wt%)	0.02	0.03

Gas C <sub>1</sub> -C <sub>4</sub> (wt%)	6.27	8.35
IBP-75 °C (wt%)	1.48	1.65
75-175 °C (wt%)	7.06	8.8
175-350 °C (wt%)	22.26	21.69
350-370 °C (wt%)	4.2	4.25
370+ °C (wt%)	23.28	23.22
Coke (wt%)	34.65	30.99

In a preferred embodiment the present invention provides a process for reducing sulphur content of heavy products obtained during a petroleum refining/petrochemical process (e.g. fuel oil, gas oil, coke, and the like).

This can also be deduced from the results described above. As a matter of fact, by favouring cracking of heavy molecules to light products, compounds under present invention contribute to reduce sulphur content of heavy products, in that sulphur will not be any more "enclosed" inside an heavy molecule, but can be "freed" during cracking.

A further preferred embodiment of present invention is coke prevention and/or yield increase during hydrocarbon pyrolysis (e.g. in ethylene production during steam cracking).

In coke formation during hydrocarbon pyrolysis methylindenes and acenaphthylene are important intermediates in coking sequences, and are for this reason good coke precursors. Coking rate increases with conversion.

As all the antifoulant compositions are formulated with heavy aromatic naphthas, and these contains indenes and naphthalenes, it can be said that the antifoulant itself can contribute, in a certain amount, to coke formation.

Coal naphtha solvent, e.g., contains in a certain amount of indane (about 30%) and naphthalenes, apart alkylbenzenes and tetralines.

As will be shown during the combustion applications of present invention, in order to reduce particulate emissions, solvent choice is of utmost importance.

Solvent of choice will have as fundamental characteristic the one of not containing any indanes and/or indenes and/or phenalenes and/or naphthalenes.

For the purposes of present invention, the additive compositions will be diluted preferably in a solvent selected from the following group: hexane, cyclohexane, benzene, toluene, xylene, cumene, MTBE, ethyl ether, diethyl ether, MEK, MIBK, GCAG, GSAG, BDM, any glycerol and/or acid oils derived as a waste and/or by-product of industrial activities.

Example 10

The charge of an ethylene plant (virgin naphtha e gas oil) was distilled; the 10% distillation residue was additivized with 1000 ppmv of various formulations. The results achieved are listed below.

Formula	CCR virgin naphtha	CCR gas oil
Blank	0,09	0,12
11244 (85% naphtha 15% pyridine)	0,02	0,06
13184 (85% BDM 15% MEK)	0,01	0,05

Coke deposits that adhere to metallic surfaces are polar in nature. The type of coke formed (compact or porous) depends upon tars rheology and from asphaltenes nature and concentration. Coke is more porous when asphaltenes have

a polycyclic non aromatic structure, and will be more compact for aromatic asphaltenes. In such a connection, the presence of polycyclic non aromatic hydrocarbons in the additive compositions under the present invention, and/or, much better, the effect of compositions under the present invention resulting in a  
5 minor asphaltenes aggregation, helps in forming a better coke, i.e. in improving coke quality.

Among the compounds claimed in present invention, nitrogen compounds in general, preferably amines, most preferably cyclic amines, contribute to variate coke morphology. Other useful compound in such connection is, e.g., toluene,  
10 which gives rise to a fibrous and needle coke.

As a further example, tetrabutylammonium hydroxide is a good swelling agent and can be effectively inserted in additive compositions under present invention in that it will contribute in changing coke morphology, creating a coke which will be more easily removed.

15 Swelling agents are well known in coal solubilization/extraction techniques, but have never been utilized petroleum/petrolchemical industry. In their known utilizations, swelling agents penetrate coal and provoke its swelling. Factors influencing the amount of swelled coal in a solvent are: a) solvent-coal interaction degree; b) cross-link density. Swelling ratio is the ratio between the volume of  
20 swelled coal, in equilibrium with the solvent, in respect to the volume of original coal.

In general, solvents utilized for such purposes posses good characteristics of coal solubilization. By using swelling agents, decoking of apparatuses, e.g. process heaters, will be eased due to change in morphology of formed coke (from "needle-  
25 like" to "fluffy" or "cloud-like").

In such connections, swelling agents can be utilized both in additive, fuel and hydrocarbon compositions under present invention to be dosed continuously in a process and/or during decoking of apparatuses, e.g. in heater decoking steam and/or in pressurized water for cleaning heat exchangers, specially for those  
30 solvents that are water-soluble.

Solvents used as swelling agents are classified in two classes: forming hydrogen bonds and non forming hydrogen bonds. In general, at this further confirms what said in this specification, the first are reported to be 25-30% as effective as the latter; effectiveness of the latter can be increased following a first coal extraction  
35 with a solvent forming hydrogen bonds with coal.

Swelling effectiveness, and hence coal penetration, is attributed to substitution of carbon-carbon hydrogen bonding with solvent-carbon hydrogen bonding: the same principle is used, among the others, in present invention.

Among non forming hydrogen bonds swelling agents are to be preferred:  
40 benzene, toluene, methyl chloride, cyclohexane, nitromethane, nitrobenzene, acetonitrile, carbon tetrachloride, naphthalene, diphenyl, xylene, tetraline, methylcyclohexane. Among forming hydrogen bonds swelling agents are to be preferred: pyridine, methanol, ethanol, ethylenediamine, propanol, 1,4-dioxane, acetone, methylene chloride, chloroform, formamide, aniline, chlorobenzene, o-  
45 dichlorobenzene, carbon disulphide, tetrahydrofuran, N,N-dimethylaniline, diethylether, dimethylsulphoxide, acetophenone, dimethylformamide, ethyl acetate, methyl acetate, methylethylketone, 1-methyl-2-pyrrolidone, quinoline.

Due to the novelty of using swelling agents in hydrocarbon processing industry, the present invention intends to cover the application of any swelling agent, known or found effective during art progresses, in additives compositions under the purposes of present invention.

5 In a further preferred embodiment the present invention provides additives compositions to achieve decoking and/or cleaning of apparatuses and/or cleaning of any material contaminated with hydrocarbons and/or petroleum products and/or fuels.

10 In such connections can also be utilized other components, according present invention, being able of solubilizing hydrocarbons and/or petroleum products and/or fuels and/or coke.

Such compounds will be injected, e.g. in heater decoking steam and/or in pressurized water for cleaning heat exchangers and/or for cleaning hydrocarbon contaminated beaches/soils/sludges.

15 In another preferred embodiment the present invention provides additives compositions to achieve cleaning of apparatuses without the need to strip the apparatus down. For example, in heat exchangers will not be necessary to extract the bundle, but cleaning will be achieved "in situ" by making flowing in them a solution (aqueous or hydrocarbyl) containing additives compositions under present invention.

20 In a further preferred embodiment the present invention provides additives compositions to achieve degassing of apparatuses. Such compositions, by solubilizing hydrocarbons, will render non explosive the atmosphere inside the apparatus and will allow a faster maintenance by avoiding long time shedules related to steam degassing.

25 A method for applying such compositions consists in the following steps: a) adding an additive composition under the present invention to a medium for dispersing and/or solubilizing it (e.g. water, steam, naphtha, gas oil, etc.); b) circulate the solution of step a) into the apparatus to be cleaned; c) repeat step a) and b), after discharging the solution of step b), until the solubilized hydrocarbon content in the solution is held constant.

30 When a water soluble additive is utilized, an advantage of such method is that solubilized hydrocarbons can be recovered, even the heavy ones, without releasing them in the atmosphere (as the case of steam degassing and/or cleaning).

35 Apparatuses to be cleaned under present invention are preferably selected from, but not limited to, the following group: petroleum refinery/petrochemical plants, oil-field plants, heat exchangers, lines, columns, desalters, flottators, API separators, storage tanks, valves, drums.

40 Always in this connection, in a further preferred embodiment the present invention provides additives compositions to reduce hydrocarbon fouling in apparatuses where hydrocarbon contaminated water flows. For example, Sour Water Stripper plant charge contain significant amounts of hydrocarbons (> 500 ppmv); such hydrocarbons cause fouling problems both in the plant itself (column, exchangers) and in downstream plants (e.g. as stripped water can be used as desalter wash water, preheat exchangers can foul).

45 Among the compounds under present invention to be used in the connections described above are to be preferred those selected from the following group:

aminoethanol, acetaldehyde, acetamide, acetic acid, ethyl acetate, acetone, acetonitrile, ethyl glycinate, amino benzoic acid, antipyrine, chlorobenzaldehyde, catechol, resorcinol, hydroquinone, benzyl alcohol, benzylamine, butylamine, dimethylglycol, butyl alcohol, methylethylketone, methylvinylketone, butyl aldehyde, butyrolactone, caprolactam, cyclohexylamine, cyclohexanol, dibutylamine, diethyleneglycol and related ethers mono- and di-butyl, mono- and di-ethyl, 1,3 and 1,4 dioxane, dipropylamine, ephedrine, ethyleneglycol, ethanol, ethanolamine, ethylenediamine, benzyl cellosolve, butylcellosolve, methylcellosolve, ethylcellosolve, formaldehyde and related diethyl-, dimethyl- and dipropyl-acetals, benzoylformaldehyde, formamide, N,N diethyl and N,N dimethylformamide, formic acid, tetrahydro-2-furanone, glycerol, hexamine, hexamethylenediamine, hexamethyleneglycol, triethanolamine, diethanolamine, imidazole, methanol, dimethylsulphoxide, morpholine, naphthalensulphonic acid, naphthoquinone, pycoline, piperazine, piperidine, propylamine, propylen glycol, propanol, propionamide, pyrazine, pyridazine, pyridine, pyrogallol, 2-pyrrolidone, N-methyl-2-pyrrolidone, quinazoline, quinossaline, tetraethyleneglycol, p-toluensulphonic acid, triethylamine, GCAG, GSAG.

Some of the above described compounds have additional features: formaldehyde, e.g., bonds  $H_2S$  and mercaptans.

#### Example 11

A beaker contained 10 g of a Vacuum distillation residue. After 5 batch washings with 10 g of hot water containing 1% methylcellosolve residue was reduce to 4 g.

As already cited, in a further preferred embodiment present invention provides additives compositions for reducing fouling in process apparatuses. An application of such invention that has been proved in laboratory is the stabilization of asphaltenes and heavy compounds present in the slurry of an FCC; HDS charges have been tested too.

#### Example 12

In 90 ml n-eptane were added 10 ml sample and then agitated for 1 minute; the mixture was allowed to stand for 15 minutes and then 70 ml of the liquid where pipetted for adding 70 ml n-eptane; solids amount (precipitated asphaltenes) was then noted. A minor amount of solids at the end of the test indicates a major asphaltenes dispersion. The additives under present invention were compared with a commercial additive of major use (Product 1). Dosage of additives was 10 ppmv. Plant charge: 56% atmospheric residue Bu-Attifel, 20 % atm. res. Amna+Sarir, 24% HVGO

Formula	Sediments (%)
Blank	9,5
Product 1	7,5
13197 (85% GCAG 15% MTBE)	5
11216 (85% Naphtha, 10% Butylglycol, 5% Atlas MC 2343)	4,5
11225 (80% Naphtha, 10% Methylglycol, 10% Solaria RS41)	6,5
12005 (85% MeOH, 15% Butylglycol)	7,5
11212 (85% Naphtha, 5% Atlas MC 2343, 10% Solaria RS41)	7

#### Example 13

- 5 Virgin naphtha charge of an HDS plant was additivized with 40 ppmv of compositions under present invention. Performance was evaluated with a thermal stability test (Admiralty Test), where a certain amount of sample is heated in a stove at 149 °C for 90 min and then filtered on Millipore AA 0,8  $\mu$  : filter pads are then compared with standard filters on a scale from 0 (clean) to 20 (black). Such test also gives an indication on oxydation stability of the sample under examination.

Formula	Evaluation
Blank	8
13216 (70% cyclohexane, 15% DEHA, 15% morpholine)	2
13217 (70% MTBE, 15% ethylenediamine, 15% xylene)	1
13168 (70% cyclohexane, 15% THF, 15% triethylamine)	0

#### Example 14

- 10 Delayed Coker heavy gas oil charge of an HDS plant was additivized with 40 ppmv of compositions under present invention. Performance was evaluated with Admiralty Test.

Formula	Evaluation
Blank	14
13178 (77% cyclohexane, 13% cyclohexylamine, 10% THF)	2
13167 (70% BDM, 15% THF, 15% triethylamine)	2

In another preferred embodiment present invention provides additive compositions for reducing coke content on catalysts, also increasing light products yields.

- 15 During processing, a little oil fraction will decompose through side-reactions and due to polymerization and condensation will form solid substances which will depose on catalyst surface, thus forming coke. Coke causes a loss in catalytic activity, via a chemical interaction with catalytic materials and block of active sites; such deactivation reduces catalyst lifetime and causes economic losses.

#### Example 15

- 20 Micro Activity Test (MAT) was performed according ASTM D 5154-92. The formula utilized was 13017= 85% MeOH 15% Imidazole , at a dosage of 1000 ppmv.

	Blank	1000 ppmv 13017
Charge	VGO 400 - 515	VGO 400 - 515
Catalyst/Oil	3,33	2,85
WHSV	14,43	16,83
Ethane (wt %)	0,51	0,62
Ethylene (wt %)	0,82	0,92
Propane (wt %)	2,40	2,56
Propylene (wt %)	6,64	7,38
iso- Butane (wt %)	8,79	9,44
n- Butane (wt %)	1,80	2,06
n- Butene (wt %)	1,37	1,66
iso- Butene (wt %)	1,48	1,40
trans-2-Butene (wt %)	2,23	2,25
cis-2-Butene (wt %)	1,57	1,61



LPG (wt %)	28,04	30,58
Gasoline [C5 -421 °F] (wt %)	61,94	57,31
LCO [421-640 °F] (wt %)	6,86	8,36
HCO [640 °F +] (wt %)	1,15	2,43
Coke (wt %)	2,05	1,41

Coke on catalyst accounts for a reduction of roughly 31%

Such application is particularly useful in hydrodesulphurization and/or hydrogenation and/or reforming plants, where operating pressure is such (generally > 5 MPa) to allow a wide choice among compounds under present invention that are in a supercritical state under normal operating plant conditions.

In a further preferred embodiment present invention provides additives compositions to decrease hydrogen make of FCC catalysts.

As a matter of facts, by favouring yield increase and less coke make, additives under present invention will not favour the dehydrogenation reactions which lead, among the others, to yield decrease and coke make, and hence to hydrogen make. Therefore, by treating the plant charge of an FCC plant with an additive under present invention there is a minor need, or no need at all, for a metall passivator additive (i.e. an additive that decrease catalyst hydrogen make).

In a further another preferred embodiment present invention provides new emulsion breakers compositions.

It is known from the art that asphaltenes and/or heavy crude fractions act as water-oil emulsion stabilizers. By solubilizing and/or stabilizing asphaltenes, the task of the active components of the emulsion breaker is eased. Addition of any compositions under present invention in the formulation of the emulsion breaker will then contribute to enhance its performance and/or to cost reduction. In particular, addition of BDM, GCAG, GSAG, MTBE, pyridine and glycol ethers proves much effective. An exemplary list of emulsion breakers active components is reported hereinafter: alcanolamines condensates, ethoxylated alcohols, ethoxylated amines, ethoxylated phenols/formaldehyde resins, ethoxylated resins, oxyalkylated phenols, polyglycols, polyglycol esters, polyhydric alcohols, sulphonic acids salts, sulfonated castor oil. Dosage of compounds under present invention effective for the purpose, vary between 1-40%, preferably 1-30%, most preferably 1-20% referred to the whole emulsion breaker formulation.

#### Example 16

20% of butylglycol was added to a commercial emulsion breaker. By evaluating the performance with a "bottle test", water drop increased from 80% of the commercial product to 95% of the modified product, and costs decreased by 15%.

In another preferred embodiment present invention provides additives compositions containing a minimum amount of an hydrogenation catalyst to favour hydrogen transfer. Such catalyst is of the oil-soluble type and contains metals such as Mo, Co, Ni. Said additives compositions will be added in the compositions under present invention in an amount sufficient to reach a final concentration from 0.0001 to 0.9 ppmw as metal, referred to the weight of the compositions under present invention.

When an hydrogenation catalyst is present in an additive composition under present invention, it will favour hydrogen transfer to asphaltenes (which agglomerates and form coke due to side chain dehydrogenation), thus avoiding dehydrogenation; the effect will be more pronounced when in the additive composition under present invention will be present an hydrogen-donor molecule, e.g. tetralin.

A further improvement of such application is to prepare the oil-soluble organometallic compound with compounds under the present invention. For example ammonium molybdate can be dissolved in a 50:50 mixture of thioglycolic acid and naphthenic acid, or in fatty acids.

The addition of an oil-soluble hydrogenation catalyst is reported in the art. Such addition is made in hydrogenation plants, where hydrogen is in ratio 100-1000:1 with charge and metal concentration is 1-1000 ppmv. The present application substantially differs from state of the art in that: a) there is no hydrogen artificially added, but the catalyst only serves to favour hydrogen transfer among the molecules, not from an hydrogen flow to molecules as in state of the art; b) the amount of active metal for the scope is far much lesser than the one used in the state of the art.

In another preferred embodiment present invention provides additives compositions for improving combustion efficiency, reducing particulate and/or soot and/or  $\text{SO}_x$  and/or  $\text{NO}_x$  and/or polycyclic aromatic hydrocarbons (PAH) emissions, maintaining clean burners and all combustion apparatuses (included boiler and heater internals), e.g. allowing a reduced amount of blowing operations. From literature data, particulate emissions increase with increasing CCR of fuel oil: in such connection additives of present invention can also be effective. In particular, will be preferred those additive compositions having GCAG and/or GSAG as solvent, in that they present technical advantages: contained methanol contribute to viscosity decrease that favours atomization; contained water contribute to particulate decrease due to "microexplosion" phenomenon. A peculiarity of GCAG and/or GSAG is that contained glycerol will favour microexplosion at a higher temperature than water: as a matter of fact, a limitation of water is that it "explodes" at low temperature; glycerol, "exploding" at higher temperature will favour more droplet core fragmentation just when particulate nucleus is being forming (i.e. at temperatures  $\geq 100^\circ\text{C}$ ), thus resulting more effective.

MTBE is also preferred as solvent in that it is a good asphaltene stabilizer, it has a low cost and contains oxygen atoms that favour combustion, apart having a very low viscosity that favours atomization.

DMF is another preferred solvent in that it is a good asphaltene stabilizer and has a low cost, apart having a very low viscosity that favours atomization; moreover, it is a known coke solubilizer, and by decomposition it forms formic acid, which is a well known compound for  $\text{NO}_x$  abatement, what results in an added value.

Compositions under present invention also contribute to  $\text{SO}_x$  and  $\text{NO}_x$  reduction by achieving a reduction in excess air, due to combustion improvement. PAH will also be reduced following asphaltenes stabilization and subsequent minor formation of heavy polynuclear compounds.

In general under present invention, oil-insoluble products can be utilized, such compounds also being oil-dispersible, and having preferably a boiling point >100 °C. In such connection it is possible to utilize compounds preferably selected from the following group: glycerol, MEA, DEA, TEA, succinimide, GCAG, GSAG, 2,3-dimethoxyaniline, 2-antraquinonsulphonic acid, 2-aminobenzamide, benzensulphonic acid, benzimidazole, benzofuran, dipyridil, putrescin (1,4 diaminobutane), butantriol, 2-caprolactone, cyclodecanol, diethyleneglycol dibenzylether, triazoethanol, N-3-tolyl-formamide, 1,2,3,4,5,6 hexanesol, hydantoin, hydroquinone dibenzoate, hexacarboxybenzenic acid, ethylmyristate, 2-amino-3-chlorophenol, 2-amino-3-nitrophenol, diaminophenol, 4-methyl-o-phenylendiamine, triethylphosphine sulfide, isobutylpyperidine, N-(2-hydroxyethyl)piperidine, 3-methylpyperidine, 1,3-diamino-2-propanol, 5-chloro-3-methyl-pyrazol, 3-methyl-1-phenyl-5-pyrazolinone, 2,4- or 3,5-diaminopyridine, 4-hydroxypyridine, methylpyrimidine, 8-aminoquinoline, resorcinol monobenzyl ether, succinic acid monomethylester, o-tolylacetic acid, 1,2,3 or 1,2,4 triazol, triisopropanolamine.

Such compounds can be directly injected in oil phase and/or dispersed in oil phase via a suitable emulsifying agent and/or injected in a suitable solvent and then dispersed in oil phase via a suitable emulsifying agent. The emulsifier can also be a part of the additive formulation.

Concerning "microexplosions" also organic nitroderivatives can be utilized, preferably the high boiling point ones (e.g. nitroalkylbenzenes), and/or any compound that explodes at boiling point and/or any other compounds under present invention. Particularly useful in such connections are substituted triazoles and tetrazoles. Compounds can be selected preferably from the following group: 2,3,4 trinitroanisoie, 1,3,5-trimethyl-2,4-dinitrobenzene, 1,3,5-trimethyl-2,4,6-trinitrobenzene, benzohydroxamic acid, 2,4,6-trinitro-m-cresol, nitroglycerol, 1,3,6,8-tetranitronaphthalene, 1,3,5-trinitronaphthalene, 2,5-dihydroxy-3,6-dinitro-p-benzoquinone, 2,4,6-trinitrophenol (pyric acid), trinitrotoluene, trinitroacetonitrile, 2,3,5-trinitro-p-xylene, substituted triazoles and/or tetrazoles with 0-2 hydrocarbyl substituents C<sub>1</sub>-C<sub>20</sub>.

#### Example 17

On a high sulphur fuel oil were made "smoke number" and effluent CO measures, by allowing its combustion in burners. Smoke numbe determination is made on a 0-10 scale; evaluations are made on a filter where gases are allowed to pass during test. A rating of 10 means a black filter, therefore, the minor the number the better the performance. CO values are expressed as ppmv on gases.

Formula	Smoke number	CO
Blank	6	130
1000 ppmv 13147 (80% GCAG 5% Pyridine 15% DMF)	1	12

In another preferred embodiment present invention provides additives and hydrocarbons compositions allowing a minor asphaltenes aggregation degree. This is particularly useful in apparatuses cleaning. For example, when a petroleum products storage tank is to be maintained, it needs a previous degassing and cleaning. Cleaning is generally a costly mechanical procedure, which implies sludge wasting. Sludge is generally made of hydrocarbons, water and sediments, all well

mixed and/or emulsified. It already exists a cleaning procedure (see Hydrocarbon Processing, January 1980) utilizing chemical dispersants to easy tank cleaning. In such connection, present invention provides additives composition that are more effective than the existing ones.

5 Example 18

To a crude oil storage tank sludge (about 200 g) were added about 2000 ppmv of formula 11200 (70% naphtha solvent 15% methylglycol 15% o-dichlorobenzene). Roughly 400 g of diluent crude were added, and the mixture maintained in agitation for 3 days (T=50 °C). After that, were added 500 ppmv of  
10 a pyridine modified emulsion breaker under present invention. The mixture was agitated for 2 days and then allowed to settle for 1 day. At the end of the procedure 3 different layers were obtained.

Parameter	Tank sludge	Formulas under pres. inv.	Commercial formulas
HC	20%	18% (water= 2% )	12% (water= 7% )
Water	75%	clean	dirty
Sediments	5%	separated	separated

In another preferred embodiment present invention provides additives, hydrocarbons and fuel compositions with reduced gaseous and/or particulate  
15 and/or soot and/or PAH emissions.

Jet fuel thermal stability will be improved too. It is measured with ASTM D 3241-92 method, where a steel rod is heated while the fluid flows at a pressure of 3.45 MPa.

Diesel fuel additives, which are based on metal salts, reduce smoke at the expense  
20 of increasing particulate emission, because the additive is emitted in the form of oxide or sulfate which contribute to the mass of particulates in the exhaust.

There remain a need for an emission-reducing additive for diesel and jet fuel that is itself metal-free and combustible without contributing to the weight of particulate emitted.

25 In another preferred embodiment present invention provides additives and "biodiesel" fuel compositions with reduced gaseous and/or particulate and/or soot and/or PAH emissions.

In a further another preferred embodiment present invention provides additives and "biodiesel" fuel compositions with reduced CCR.

30 It is known from literature that during biodiesel combustion this fuel leaves a residue of the resinous type, which creates problems both on burners and on engines (deposits on cylinder-head and on gaskets). Results obtained by present invention are extremely interesting and confirm the novelties hereinabove described.

35 As a matter of fact, if a Vacuum residue can "mask" additives effect (e.g. n-eptane precipitates asphaltenes and, when not well mixed, an evaluation on a deasphalted sample can be done), for biodiesel there are no petroleum type asphaltenes, and therefore additives effect is clearly the one of avoiding heavy molecules aggregation.

40 Test on CCR reduction were performed both on biodiesel as it is and on 10% distillation residue of diesel fuel and biodiesel. The last two test are of particular relevance, in that the distillation residue is the fuel heaviest fraction, which will

predominantly contribute to CCR formation and hence to particulate and/or soot and/or unburnt hydrocarbons emissions. By reducing this parameter an emissions reduction will occur.

- 5 In additives formulations under this connection, "supercritical" compounds under present invention can also be added, in that pressure inside the engine is often >7 MPa, thus permitting a wide product choice.

Diesel fuel used for tests had the following characteristics:

Sp.gr. @ 15 °C	0,8458	CFPP (°C)	-5	Visc. @ 100 °C	3,2
ASTM Dist.		P.M. (°C)	76	Tot. ac.	0,04
IBP	187	S (wt %)	0,22	Exist. sed.	0,4
%v @ 250°C	18	C. P. (°C)	+2	Pot. sed.	0,5
%v @ 300°C	65	P.P. (°C)	-9	Cu corr.	1A
%v @ 350°C	96	ASTM Colour	1		
10% (°C)	237	BS&W (%v)	0		
50% (°C)	283	Diesel Index	1		
90% (°C)	341	Ash (wt %)	0,001		
95% (°C)	365	Cetane number	53		

In the reduction of CCR on diesel and/or biodiesel fuel a further novelty is the type of solvent utilized in the formulation of additives.

- 10 As the additives compositions are normally formulated with heavy aromatic naphthas, and these contains indenenes and naphthalenes, it can be said that the additive itself can contribute, in a certain amount, to emissions. Coal naphtha solvent, e.g., contains in a certain amount of indane (about 30%) and naphthalenes, apart alkylbenzenes and tetralines.

- 15 Indane is reported in the literature as responsible of diesel fuel sediment formation, in that it combines with phenanelone; moreover it is known that nitrogen compounds also contribute to sediment formation.

In this connection, the formulations used to reduce sediment formation in gas oil plant charge described above, can be suitably modified.

- 20 Solvent of choice will have as fundamental characteristic the one of not containing any indanes and/or indenenes and/or phenalenes and/or naphthalenes.

Preferred solvents in this connection can be selected from the following group: biodiesel, cyclohexane, MTBE, THF, paraffinic solvents, no solvent.

- 25 In another preferred embodiment present invention provides additives compositions to be utilized without any solvent, only injecting the active portion of the additives.

This application has an added value in that it allow to spare on trasport costs, thus decreasing global costs of additives.

Example 19

- 30 Diesel fuel above reported was distilled to recover 10% residue, which was subsequently additivized with 1000 ppmv of additives under present invention and analyzed for CCR.

Formula	CCR
Blank	0.06
13168 (70% cyclohexane 15% THF 15% triethylamine)	0.03

13165 (85% BDM 15% THF)	0.02
13053 (70% water 15% DEA 15% DEHA)	0.03

## Example 20

An engine test was performed by utilizing a Fiat Tipo D car (diesel engine 1700 cc) at full load and variable speed. Test was performed with a diesel fuel as it is and with a diesel fuel additivized with 500 ppmv of formula 13165, evaluating fuel consumption in both cases.

Engine speed (rpm)	Cons. w/o add.(g/Kw-h)	Cons. with add.(g/Kw-h)
1000	241	230
1600	218	215
2200	222	219

Exhaust emissions have also been evaluated during engine run. It was found that HC emissions were reduced from 0.652 g/CV-h without additive to 0.498 g/CV-h with additive; particulate emissions were reduced from 0.365 g/CV-h without additive to 0.297 g/CV-h with additive. All those reductions were achieved without significant changes in NO<sub>x</sub> and CO emissions.

PAH emissions was also evaluated, in terms of ng PAH/mg particulate emissions. Average results for the fuels at two dynamometric load levels, with engine operating at 1560 rpm, are listed below.

	Engine load 50%	Engine load 75%
Fuel w/o additive	610	1200
Fuel with additive	320	615

A qualitative evaluation was also made on some engine parts after 60,000 Km run with additivized fuel: injectors, preheat candles, cylinder wall internals all were very clean and in a good state.

Additives under present invention decrease exhaust smoke, improve combustion effectiveness, reduce fuel consumptions and engine fouling, and reduce emission levels.

In another preferred embodiment present invention provides additives and fuel compositions with a minor CCR.

It was already seen that additives compositions under present invention act in the sense of CCR reduction. This is interesting not only because CCR influences emissions, but also because CCR is a commercial specification for fuels. It follows then, that additives under present invention can also be used for maintaining within specification an out of spec fuel.

Particular is the case of vegetable diesel fuels (that generally have a CCR higher than petroleum diesel fuels) and petroleum diesel fuels, where CCR is measured after distillation of the fuel in 10% distillation residue. For these fuels, compounds under present invention to be utilized are preferably those having a boiling point in the range 200-500 °C, most preferably 300-400 °C.

An exemplary list of such compounds can be found in the Handbook of Chemistry and Physics 74<sup>th</sup> Edition -CRC Press-, pages 3-12 through 3-523. Among these compounds are to be preferred those selected from the following group:  $\beta$ -antraquinoline, antraquinone, antipyrine, eicosanol, benzalacetophenone, 2-nitrobenzamide, benzanthrane, 1-chloro-2,6-dinitrobenzene, hydroquinone, p-dinitrobenzene, 1,3,5 trimethyl-2,4 dinitrobenzene, dodecylbenzene,

- hexachlorobenzene, hexaethylbenzene, hexamethylbenzene, nonylbenzene, 1,2,3-triaminobenzene, 1,2,3-trihydroxybenzene, 1,3,5-triphenylbenzene, p-benzidine, benzyl, 1-methylbenzimidazol, 2-benzoylbenzofuran, benzoic anhydride, 2-benzoyl-methyl benzoate, benzyl benzoate, 4-tolyl benzoate, 2-phenoxybenzoic acid, benzoine, benzophenone, 4,4'-bis(dimethylamino), 4-chlorobenzophenone, 4,4'-chlorobenzophenone, 2,2'-dihydroxybenzophenone, 2,2'-dimethylbenzophenone, 4,4'-dimethylbenzophenone, methylbenzophenone, 1,2 benzopyrene,  $\beta$ -naphthoquinoline, 2-methyl- $\beta$ -naphthoquinoline, 2-hydroxybenzothiazol, 2-phenylbenzothiazol, 2-amino benzylic alcohol, 3-hydroxy benzylic alcohol,  $\alpha$ -1-naphthyl benzylic alcohol, benzyl-ethyl-phenyl-amine, benzylaniline, benzyl ether, phenylacetophenone, 2-acetamide diphenyl, 2-amino diphenyl, 4,4'-bis(dimethylamino) diphenyl, diphenol, dianisol, butyl-bis(2-hydroxyethyl)amine, butylphenylamine, butylphenylketone, carbammic acid, carbazol, 1,2,3,4 tetrahydrocarbazol, diphenylcarbonate, cetyl alcohol, cetylamine, cinnamic acid, benzylcinnamate, coronene, coumarine, lindan, dicarboxylic acid of cyclohexane, dibenzofuran, dibenzothiophene, dibenzylamine, diethylene glycol dibenzyl ether, diethylene glycol monolaurate, diethylene glycol (2-hydroxypropyl) ether, diethylenetriamine, di- $\alpha$ -naphthylamine, di- $\alpha$ -naphthylamine methane, di- $\beta$ -naphthylamine, dioctylamine, diphenylamine, diphenyl disulphate, 4,4'-diamino diphenyl, 4,4'-dimethylamino diphenyl, 4-hydroxy diphenyl, diphenyl methanol, diphenyl ethylamine, diphenylsulphide, di-( $\alpha$ -phenyl ethyl)amine, di-isopropanolamine, di-2-tolylamine, 4,4' ditolylsulphate, eicosanol, 1,1,2 triphenylthane, ethylene glycol 1,2 diphenyl, ethyl-di-benzylamine, ethylene glycol monobenzyl ether, ethylene glycol monophenyl ether, fluorene, N,N-diphenylformamide, phenylformamide, tolylformamide, 2-benzoylfuran, 2,5 diphenylfuran, glycerol and related esters, eptadecylamine, eptadecanol, cerilic alcohol, hexadecanamine, hydroxyethyl-2-tolylamine, triethanolamine, imidazole, methylimidazole, phenylimidazole, 5-amino-indane, 5-esyl-indane, 1-phenyl-1,3,3-trimethyl-indane, indanole, indazole, 2,3 diphenyl-indene, indole, 2,3 dimethyl-indole, triptamine, 2-phenyl-indole, isocoumarine, isonicotine, diethyl-isophthalate, isoquinoline, benzyl laurate, phenyl laurate, lauryl alcohol, lauryl amine, lauryl sulphate, diethyl-benzyl-malonate, melamine, diphenyl methane, triphenyl methane, 4-benzyl-morpholine, 4-phenyl-morpholine, 4-(4-tolyl)-morpholine, myristic alcohol, 9,10-dihydro-naphthalene, acetyl-naphthalene, benzyl-naphthalene, butyl-naphthalene, chloronitro-naphthalene, dihydro-naphthalene, dihydroxy-naphthalene, dinitro-naphthalene, methyl-naphthalene, nitro-naphthalene, phenyl-naphthalene, naphthoic acid, naphthol, naphthylamine, methylnaphthylamine, naphthylphenylamine, naphthylsulphide,  $\alpha$ -naphthyl-2-tolyl-ketone, methyl or ethyl ester of nitrobenzoic acid, 3-nitrobenzamide, nonacosanol, octadecanol, octyl-phenyl-ether, pentadecylamine, pentadecanol, phenanthrene, hexahydrophenanthrene, octahydrophenanthrene, phenanthroline, phenanthroquinone, phenazine, 3-hydroxyacetophenone, 2-benzylphenol, p-cycloesylphenol, m-phenylphenol, phenothiazine, 4-hydroxyphenylacetoneitrile, o-phenylenediamine, N-phenyl-phenylenediamine, 4-methyl-phenylenediamine, diphenyl ether, bis-(2-phenyl ethyl)amine, phenylhydrazine derivatives such as benzoyl, sulphide, sulphone and sulfoxide, phosphine derivatives such as phenyl,

triphenyl and oxide, triphenylphosphite, acid esters such as dibutyl, dibenzyl, diethyl and diphenyl, phthalic anhydride, 3,5 dichloro phthalic anhydride, N-benzoylpyperidine, 1,3-diphenoxypropane, N-(2-tolyl)propionamide, 1-methyl-3-phenyl-pyrazoline, pyridine derivatives such as 3-acetamido, 3-benzyl, 4-hydroxy, 2-phenyl, pyrogallol, catechol, quinazoline, quinazolinone, quinoline and its derivatives such as 2-amino-4-methyl, 4-amino-2-methyl, 5-amino, 2-hydroxy-4-methyl, 6-hydroxy, 8-hydroxy, 2-phenyl, resorcine, 4-esylresorcine, retene, salicylic acid and related benzylic e methyl esters, phenylsuccinic anhydride, succinimide, N-benzylsuccinimide, N-phenylsuccinimide, tartaric acid esters such as dibenzyl and dibutyl, o-terphenyl, m-terphenyl, 1,14 tetradecandiol, tetradecanol, tetraethyleneglycol, tetraethylenepentamine, 2,4-diphenyl thiazole, 2-methyl-5-phenyl thiophene, tetraphenyl thiophene, 2,5-diaminotoluene, 3,5-dihydroxytoluene, 4-phenyl toluene, p-toluensulphonic acid and related methyl and propyl esters, o-toluic acid and related anhydride, N-benzyl-toluidine (o-, m- e p-), 4-tolyl-sulphone, 1,2,4 od 1,2,3 triazole, tribenzylamine, tributylamine, triethanolamine, triethyleneglycol and related monobutylether, triethylamine, trioctylamine, triphenylamine, trithiane, tritanol, 2-pyrrolidone, xanthene, xanthone, nitroxyls, xylydine.

A compound of particular effectiveness is a fatty amines mixture handled under the trade name Solaria RS 41 from BP Chemicals: 50% of such product has a boiling point > 310 °C and falls then under the purposes of present invention. The same for any commercial mixture of fatty amines or single fatty amine.

#### Example 21

A petroleum diesel fuel had a CCR of 0.09% on 10% distillation residue. By adding 1000 ppmv of formula 13198 (75% cyclohexane, 5% DEHA, 10% THF, 10% Morpholine) CCR value was brought to 0.02%

#### Example 22

A vegetable diesel fuel (rapeseed oil methylester) had a CCR of 0.24% on 10% distillation residue. By adding 1000 ppmv of formula 13113 (85% Naphtha 15% Solaria RS41) CCR value was brought to 0.10%. By adding 1000 ppmv of formula 13037 (85% Naphtha 15% Triethyleneglycol) CCR value was brought to 0.10%.

In another preferred embodiment of present invention, operating process conditions can be varied to bring in a supercritical state additives compositions that are not supercritical at normal operating conditions.

For example, heater coil pressure can be brought from 14 bar to, e.g., 25 bar for making possible utilizing p-toluidine, hexamethylbenzene, etc..

Compounds under present invention can also be used during fuel combustion in an apparatus that brings them in a supercritical state, to reduce particulate and/or soot and/or SO<sub>x</sub> and/or O<sub>x</sub> and/or PAH.

In a further preferred embodiment the present invention provides additives compositions to pretreat a plant charge. This can be the case, e.g., of the charge to a catalytic plant to achieve a better penetration of the charge in the catalyst. Plant like, e.g., Catalytic Hydrocracking, Residue Demetallation, Reformers, Fluid Catalytic Cracking, etc., are all benefited in such connection.

In another preferred embodiment the present invention provides additives and hydrocarbon compositions with improved rheological properties. This becomes evident from Example 3.



It is now known that the presence of paraffinic components in petroleum compositions contribute to worsen their rheological properties. In such connection, adding non paraffinic components in the formulation of, e.g., a fuel oil help decrease its pour point. Such operation is well known in the art, but it is difficult to realize due to compatibility problems among the different fractions.

As present invention solves said compatibility problems, it will be possible having more blending possibilities to satisfy rheological properties. Example 3 confirms the above, as evident from Pour Point and viscosity analysis: by adding an asphaltenic residue to a paraffinic one, Pour Point and viscosity of the paraffinic residue decrease significantly: this can be done without compatibility problems.

Present invention is also useful for separating organics from solid wastes and hazardous wastes (e.g. petroleum waste, refinery sludge, and the like). It is also suitable for extracting oil from oil-contaminated catalyst fines, filter aids, drilling cuttings, steel mill waste, bleaching clay, etc. The process is also useful for cleaning filter beds, waste-contaminated soils, etc., and for extracting bitumen from tar sands. This all can be done without being in supercritical conditions by contacting, e.g., wastes with an aqueous solution of a compound under present invention.

Present invention is also useful for reducing viscosity of fuels and of waste materials.

In a further preferred embodiment, the present invention provides a process, a method and additives compositions for preventing oil destabilization during processing. This is of utmost importance for crude oils, fuel oil and bunker oils. Nowadays, while crude oils and fuel oils are well tabulated and well localized in the market, there is a need in the art to avoid incompatibility problems of bunker oils. As a matter of facts, ships get fuel supplies in different places, where fuel quality is not always appropriately controlled and where there is no means for avoiding stability and/or compatibility problems: the result is difficulties in engine operation and/or plugging of apparatuses.

The same for crude oils and/or fuel oils that can be present incompatibility problems following their storage and/or blending. It follows the need in the art for a method for preventing any stability problem, specially if this method is easily applicable by use of an additive to be injected in the oil.

#### Example 23

A bunker oil had an HFT= 0.23 %. The addition of 1000 ppmv of formula 13201 (85% GCAG 15% TEA) resulted in a reduced HFT=0.08 %

#### Example 24

A bunker oil had a CCR= 19.4 %. The addition of 1000 ppmv of formula 13224 (85% GCAG 15% Linear Alkyl Benzene C10-13) resulted in a reduced CCR=16.8 %.

In a further another preferred embodiment, the present invention provides a process, a method and additives compositions for improving coke and/or coal combustion efficiency.

As coke is composed of asphaltenes molecules lying in stacked layers and much of the additive compositions under present invention are even able to solubilize coke, it is evident that under present invention coke will burn more effectively.

This, in turn will induce a minor particulate emission during coke combustion.

#### Example 25

Petroleum coke derived from a Delayed Coking plant (about 5 g) was additivized with 1000 ppmv of formula 13240 (50% naphtha solvent 50% MTBE) and then allowed to burn in a muffle. By making tests of combustion speed, a definite amount of coke was posed on a crucible and then in a muffle set at 800 °C; at different times the crucible was taken out of the muffle and reweighed for calculation of residual coke. In another test, the crucible was held for 1 hour at a defined temperature and then reweighed for calculation of residual coke. The results are reported below.

	Residual coke at varying times	
Time	Blank	1000 ppmv 13240
1h 30'	87%	72%
2h 30'	47%	21%
3h 45'	33%	13%
4h 30'	23%	1%

	Residual coke at varying temperatures	
Temperature	Blank	1000 ppmv 13240
500 °C	92%	81%
600 °C	55%	22%
700 °C	38%	1%
800 °C	28%	0.8%

Without wishing to be bound to any specific ratio among the components, additive formulations under present invention can be in the following ranges: solvent 0-100%, active components 100-0%; preferably: solvent 50-90%, active components 10-50%; most preferably: solvent 30-80%, active components 20-70%.

Generally speaking, additives under present invention are preferably obtained by blending among compounds hereinabove described, and not by their reaction under specified conditions.

From what seen in this specification, applications of present invention are multiple; the same for operating conditions in utilizing it.

In general, operating temperatures will vary between 1-2000 °C, preferably 1-1300 °C, most preferably 1-900 °C; pressure will vary between 0.001-15 MPa, preferably 0.01-8 MPa, most preferably 0.1-5 MPa.

Typical dosages of additives under present invention can vary between 1-20000 ppmv in weight referred to the material to be treated, preferably 50-8000 ppmv, most preferably 100-4000 ppmv.

It is obvious to the skilled in the art that amount of additives to be utilized under present invention will be dependent upon hydrocarbon and/or fuel and/or residue types and/or operating conditions and/or results to be obtained.

Present invention will not be limited by any specific amount of additive to be utilized, although this parameter must be substantially within the ranges above described. The same for operating conditions of present invention.

As all asphaltenic molecules are complex and different in nature, their structure will be variable and non preventable, and will be difficult to define an additive composition under present invention that will perform well with all, e.g., residues, fuels, crudes to which this invention pertains and can effectively be employed.

5 Without departing from general principles and dosages defined in present invention, the best way for determining the best composition for a specific embodiment under present invention is to determine case by case what performs better.

10 The hydrocarbon oil compositions to which present invention refers are selected preferably from the following group: unrefined and refined hydrocarbonaceous products derived from petroleum or from liquefaction of coal, both of which contain sulfur compounds; wellhead condensate as well crude oil which may be contained in storage facilities at the producing field and transported from those facilities by barges, pipelines, tankers, or trucks to refinery storage tanks, or,

15 alternatively, may be transported directly from the producing facilities through pipelines to the refinery storage tanks; refined products, interim and final, produced in a refinery, including distillates such a gasolines, naphthas, gas oils, distillate fuels, oils, residues, residual fuels, fuel oils, diesel fuels and plant charges; petroleum gases, methane, ethane, propane, butane, ethylene, propylene; coke

20 and/or coal derived from petroleum refining and/or from mining .

Concerning the acid vegetable and/or aimal and/or industrial oils derived as a by-and/or waste- product of industrial activities, the oils of choise are preferably selected from the following group: crude and/or distilled tall oil, castor oil, acid seed oil (of any kind of seed), acid olive oil.

25 Concerning the preparation of soluble hydrogenation catalysts under present invention, the compositions are preferably selected from the following group: i) a reaction product between a molybdenum compound selected from the group:  $\text{MoCl}_3$  ,  $\text{MoCl}_2$  ,  $\text{Mo}_2\text{O}_3$  ,  $\text{MoO}_2$  ,  $\text{Mo}_2\text{O}_5$  ,  $\text{MoP}_2$  ; and an acidic type compound selected from the group: GCAG, fatty acids, carboxylic acids, any acid vegetable and/or aimal and/or industrial oil derived as a by-and/or waste-product

30 of industrial activities (e.g. crude and/or distilled tall oil, castor oil, acid seed oil, acid olive oil, etc.); ii) a molybdenum compound selected from the group:  $\text{Mo}(\text{CO})_6$  ,  $\text{MoO}_2\text{Cl}_2$  ,  $\text{Mo}_2\text{O}_3\text{Cl}_6$  ;  $\text{MoO}(\text{OH})_2\text{Cl}_2$  , dissolved in a compound under present invention.

35 Without departing from the scopes of present invention, all the compositions specified can also contain amounts, sufficient to the scope, of active ingredients already known in the art. The addition of any dispersant, asphaltene stabilizer, combustion catalyst, detergent in the formulations under present invention cannot prejudice the novelty of the present invention.

40 Likewise, additives under present invention can be used alone, as a unique additive in a compositions, or in combination with other known additives, like, e.g., pour point depressants, CFPP depressants, antifoulants, emulsion breakers, antifoamers, emulsifiers, neutralizers, corrosion inhibitors, antioxydants, sludge inhibitors, and the like.

45 In the above specification, all data obtained during lab tests and experiments have been included for completeness. Efforts to exclude any value outside acceptable error limits have not been made. It is believed that, during course of

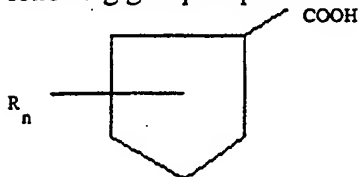
these tests and experiments, possible errors in preparing samples and in making measurements may have been made which may account for any occasional data that is not supportive of this art.

5 While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth hereinabove but rather that the claims are construed as encompassing all the  
10 features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

## CLAIMS

- 1) Hydrocarbon oil and/or aqueous and/or fuel and/or additives compositions comprising at least one of the following properties:
- stabilization and/or reeptization of asphaltenes;
  - fouling and/or coke reduction in apparatuses where those compositions flow;
  - HFT and/or CCR reduction;
  - rheological properties improvement;
  - conversion and/or distillation yield increase;
  - fouling and/or coke formation reduction on catalysts;
  - particulate and/or soot and/or  $\text{SO}_x$  and/or  $\text{NO}_x$  and/or PAH reduction during combustion;
  - improved stability and/or compatibility;
  - new types of solvent presence and/or high performances with respect to properties from a) to h).
- 2) Compositions according to claim 1 having: i) improved stability and/or reeptization of asphaltenes and/or ii) improved stability to blending operations and/or iii) minor HFT and/or CCR and/or Pour Point and/or viscosity.
- 3) Compositions according to claim 2 comprising one or more additives.
- 4) Additive according to claim 3 wherein formulations will contain one or more compounds selected from the following group: glycol of general formula  $\text{CH}_2\text{OH}-(\text{CH}_2)_n\text{OH}$  where  $n=0-10$ ; glycol ethers of general formula  $\text{R}_1\text{-O-CH}_2\text{-CH}_2\text{-O-R}_2$  where  $\text{R}_1$  is an hydrocarbyl substituent  $\text{C}_1\text{-C}_{20}$  and  $\text{R}_2$  is H atom or an hydrocarbyl substituent  $\text{C}_1\text{-C}_{20}$ ; glycol esters of general formula  $\text{R}_1\text{-O-O-CH}_2\text{-CH}_2\text{-O-O-R}_2$  where  $\text{R}_1$  is an hydrocarbyl substituent  $\text{C}_1\text{-C}_{20}$  and  $\text{R}_2$  is H atom or an hydrocarbyl substituent  $\text{C}_1\text{-C}_{20}$ ; thioglycols of general formula  $\text{HO-R}_1\text{-S-R}_2\text{-OH}$  where  $\text{R}_1$  is an hydrocarbyl substituent  $\text{C}_1\text{-C}_{10}$  and  $\text{R}_2$  is H atom or an hydrocarbyl substituent  $\text{C}_1\text{-C}_{10}$ ; glycol ethers-esters of general formula  $\text{R}_1\text{-O-CH}_2\text{-CH}_2\text{-O-O-R}_2$  where  $\text{R}_1$  and  $\text{R}_2$  are an hydrocarbyl substituent  $\text{C}_1\text{-C}_{20}$ ; halogenated hydrocarbons of general formula  $\text{R-X}_n$  where  $\text{R}$  is an hydrocarbyl substituent  $\text{C}_1\text{-C}_{20}$ ,  $\text{X}$  is indifferently the atom Cl, F, Br, I and  $n=1-10$ .

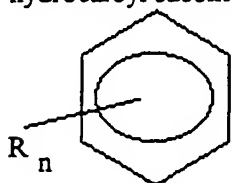
Other compounds according the present invention can be selected from the following group: naphthenic acids of general formula



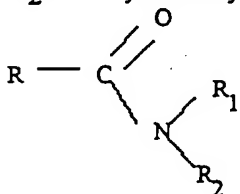
where  $\text{R}$  is an hydrocarbyl substituent  $\text{C}_1\text{-C}_{20}$  and  $n=0-4$ ; substituted esters of general formula  $\text{R}_1\text{COOR}_2$  where  $\text{R}_1$  or  $\text{R}_2$  is an hydrocarbyl substituent  $\text{C}_1\text{-C}_{20}$ ; amines and ammonium salts of general formula



- where R and R<sub>1</sub> are indifferently H atom, -OH group or an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>, R<sub>2</sub> the group -OH or an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>; nitriles of general formula R-CN where R is an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>; carboxylic acids of general formula RCOOH where R is an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>; alcohols of general formula R-OH where R is an hydrocarbyl substituent C<sub>1</sub>-C<sub>40</sub>; ethers of general formula R<sub>1</sub>-O-R<sub>2</sub> where R<sub>1</sub> or R<sub>2</sub> is an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>; acetates of general formula CH<sub>3</sub>COOR where R is an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>; formates of general formula HCOOR where R is an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>; substituted benzenes of general formula



- where n=1- 6 and R can be indifferently H atom, -OH group, -COOH group, -CHO group, -NO<sub>2</sub> group, -NH<sub>2</sub> group, -SH group, -HSO<sub>3</sub> group, the same or different hydrocarbyl substituent C<sub>1</sub>-C<sub>30</sub>; ketons of general formula R<sub>1</sub>-CO-R<sub>2</sub> where R<sub>1</sub> or R<sub>2</sub> is an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>; sulfones of general formula R<sub>1</sub>-SO<sub>2</sub>-R<sub>2</sub> where R<sub>1</sub> or R<sub>2</sub> is an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>; sulfides of general formula R<sub>1</sub>-S-R<sub>2</sub> where R<sub>1</sub> or R<sub>2</sub> is an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>; sulfoxides of general formula R<sub>1</sub>-SO-R<sub>2</sub> where R<sub>1</sub> or R<sub>2</sub> is an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>; anhydrides of general formula R<sub>1</sub>-CO-O-CO-R<sub>2</sub>, included those where R<sub>1</sub> and R<sub>2</sub> are bound together to form cyclic anhydrides, where R<sub>1</sub> or R<sub>2</sub> is an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>; amides of general formula



- where R, R<sub>1</sub>, R<sub>2</sub> are indifferently H atom or an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>; thiolamines of general formula NR<sub>1</sub>R<sub>2</sub>SH where R<sub>1</sub>, R<sub>2</sub> are indifferently H atom or an hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>; hetherocyclic compounds, preferably the hydrogenated ones, containing from 0 to 3 hydrocarbyl substituent C<sub>1</sub>-C<sub>20</sub>, selected preferably from the following group: furans, thiophene, pyrrols, pirazoles, imidazoles, triazoles, dithiols, oxathiol, oxazoles, thiazoles, oxadiazoles, oxatriazoles, dioxazoles, oxathiazole, pyranes, pyrones, pyridine, pyridazine, pyrimidine, pyrazine, piperazine, piperidine, triazines, oxazines, oxathiazines, oxadiazines, morpholine, azepine, oxepin, thiepin, diazepine, indane, indenenes, benzofuranes, benzothiophenes, indoles, pyrane-pyrrole, indazole, indoxazine, benzoxazole, anthranile, benzopyrane, coumarines, quinolines, benzopyrones, cinnoline, quinazoline, naphthyridine, pyrido-pyridine, benzoxazines, carbazole,

xanthene, acrydine, purine, benzopyrroles, benzothiazoles, cyclic amides, benzoquinolines, benzocarbazoles, thioquinolines, indolothiophenes, carbazothiothiophenes, indoline, benzotriazoles.

- 5) Additives according to claim 4 wherein active compounds are preferably selected from the following group: trichloroethylene, tetrachloroethylene, methanol, ethanol, propanol, isopropanol, butanol, isobutanol, methylglycol monomethylether, butylglycol monobutylether, toluene, heavy amines (e.g. Solaria RS41, BP Chemicals), aryl sulfonates (e.g. Atlas MC 2343, ICI), glycerol, thioglycolic acid, naphthenic acid, o - dichlorobenzene, benzene, anthracene, carbon tetrachloride, carbon sulfide, pyridine, aniline, chloroform, tetraline, 1-methylnaphthalene, diphenyl, phenanthrene, o-cresol, phenol, nonylphenol, 1-methyl-2-pyrrolidinone, diethyl ether, dimethylformamide (DMF), tetrahydrofuran (THF), ethylenediamine, diethylamine, triethylamine, propylamine, 1-(3-aminopropyl)-2-pyrrolidone, 1-(3-aminopropyl) imidazole, N-hydroxyethyl-imidazolidinone, N-aminoethyl-imidazolidinone, 2-(2-aminoethylamino)ethanol, furfurylamine, isopropylamine, cumene, 1,3,5 trimethylbenzene, 1,2,4 trimethylbenzene, indane, tetrahydroquinone, 4-hydroxyindane, ammonium octanate, maleic anhydride, tetrabutylammonium hydroxyde, thiophenol, p-toluidine, o-toluidine, thiophene, dipropylamine, quinoline, isoquinoline, tetrahydroquinoline, diphenyl ether, hexamethylbenzene, propylbenzene, cyclohexylamine, 1-isopropyl-4-methyl-benzene, 1,2,3,5 tetramethylbenzene, isoamyl acetate, carbohydrazide, hydroquinone, diethylhydroxylamine (DEHA), hexanol, tetrahydrothiophene, morpholine, nitrobenzene, o-xylene, m-xylene, p-xylene, 2-mercaptobenzothiazole, butylamine, methylamine, p-chlorothiophenol, 5,6 dihydro-4-methylpyrane, 2-methylfuran, benzothiophene, benzophenone, piperazine, piperidine, mesitylene, hexamine, succinic anhydride, decahydronaphthalene, ethylbenzene, 1,2 dimethylnaphthalene, 1,6 dimethylnaphthalene, p-cymene, ethyl ether, isopropyl ether, etoxybenzene, phenyl ether, acetophenone, o-chlorotoluene, m-dichlorobenzene, monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), cis-decaline, trans-decaline, diethyleneglycol, triethyleneglycol, tetraethyleneglycol, dodecylbenzene, lauryl alcohol, myristyl alcohol, salicylic acid, 8-hydroxyquinoline, benzotriazole, tolyltriazole, thiodiglycol, salicylic aldehyde, p-toluensulphonic acid, dibutylphthalate, dinonylphthalate, methylethylketone (MEK), methylisobutylketone (MIBK), methyl-tert-butyl-ether (MTBE), sulfolane, cyclohexane, 3,6-dioxyphtalimide, 3,6-tetramethyldiaminoxantone,  $\alpha$  naphthylamine,  $\beta$  naphthylamine, acrydine, fluorescein, coumaric acid, 1-naphthol-4-sulphonic acid, 2-naphthol-3,6-disulphonic acid, naphthothionic acid,  $\beta$  naphthol,  $\alpha$ -naphtholsulphonic acid, 1,4-naphtholsulphonic acid, coumarine, mixtures methanol/KOH, 2-aminoethanethiol, dimethylaminothiol, diethylaminothiol, mixtures of esters derived from fatty acids transesterification (biodiesel), glycerol derived as a by-product of fatty acids transesterification (with or without dissolved fatty acid and/or alcohol (GCAG or GSAG)), any glycerol derived as a by-product of industrial activities (e.g. the ones derived from the production of soap and/or fatty acids), any acid vegetable and/or animal and/or industrial oil derived as a by-

and/or waste-product of industrial activities (e.g. crude and/or distilled tall oil, castor oil, tallow oil, acid seeds oil, acid olive oil, etc.).

6) Additives according claims 4 and 5 wherein solvents are selected preferably from the following group: hexane, benzene, methanol, ethanol, propanol, MTBE, cyclohexane, cumene, toluene, xylene, ethyl ether, diethyl ether, glycol ethers, MEK, MIBK, mixtures of esters derived from fatty acids transesterification (biodiesel), glycerol derived as a by-product of fatty acids transesterification (with or without dissolved fatty acid and/or alcohol (GCAG or GSAG)), any glycerol derived as a by-product of industrial activities (e.g. the ones derived from the production of soap and/or fatty acids), any acid vegetable and/or animal and/or industrial oil derived as a by-and/or waste-product of industrial activities (e.g. crude and/or distilled tall oil, castor oil, tallow oil, acid seeds oil, acid olive oil, etc.); or wherein there is no solvent.

7) Compositions according to claim 1 wherein hydrocarbons are selected preferably from the following group: unrefined and refined hydrocarbonaceous products derived from petroleum or from liquefaction of coal, both of which contain sulfur compounds; wellhead condensate as well crude oil which may be contained in storage facilities at the producing field and transported from those facilities by barges, pipelines, tankers, or trucks to refinery storage tanks, or, alternatively, may be transported directly from the producing facilities through pipelines to the refinery storage tanks; refined products, interim and final, produced in a refinery, including distillates such as gasolines, naphthas, gas oils, distillate fuels, oils, residues, residual fuels, fuel oils, diesel fuels and plant charges; petroleum gases, methane, ethane, propane, butane, ethylene, propylene; coke and/or coal derived from petroleum refining and/or from mining.

8) Compositions according to any of the claims 1-7 which give rise to: i) minor fouling and/or minor coke formation in the apparatuses where they flow and/or are contained and/or ii) increased conversion yields and/or iii) minor coke formation on catalysts and/or iv) minor gaseous and/or particulate and/or soot emissions.

9) Compositions according to claim 8 comprising an additive selected from the group of claim 4.

10) Compositions according to claim 9 comprising an additive according to claim 5,6.

11) Compositions according to claim 9-10 comprising an additive which is in supercritical state at normal operating conditions of apparatuses where such compositions flow and/or are contained.

12) Compositions according to claim 9-10 comprising an additive with critical pressure  $< 8$  MPa, preferably  $< 5$  MPa, most preferably  $< 3.5$  MPa and with critical temperature  $> 200$  °C, preferably between  $200$  °C and  $600$  °C, most preferably between  $400$  °C and  $500$  °C.

13) Additive according the claims 11-12 wherein active components are selected preferably from the following group: tetrachloromethane, dimethylamine, ethylamine, ethyl formate, methyl acetate, dimethylformamide, propanol, propylamine, isopropylamine, trimethylamine, tetrahydrofuran, ethyl vinyl ether, ethyl acetate, propyl formate, butanol, methyl propanol, diethyl ether, methyl propyl ether, isopropyl methyl ether, diethyl sulfide, butylamine, isobutylamines, diethylamine, cyclopentanol, pentanones, 2-methyltetrahydrofuran,



tetrahydropyran, pentanal, butanoic acids, isobutyl formate, propyl acetate, pentanoic acid, butyl methyl ether, tert-butyl methyl ether, ethyl propyl ether, bromobenzene, chlorobenzene, aniline, methylpyridines, cyclohexanone, cyclohexane, methylcyclopentane, cyclohexanol, hexanal, pentyl formate, isobutyl acetate, 2-ethoxyethyl acetate, methyl pentyl ether, dipropyl ether, diisopropyl ether, hexanol, methyl pentanols, triethylamine, dipropylamine, diisopropylamine, benzonitrile, benzaldehyde, toluene, cresols, benzyl alcohol, methylanilines, dimethylpyridines, furfural, pyridine, methylcyclohexane, heptanol, acetophenone, ethylbenzene, xylenes, ethylphenols, xyenols, anilines, heptanol, acetophenone, ethylbenzene, xylenes, ethylphenols, xyenols, dimethylaniline, ethylaniline, octanenitrile, ethyl propanoate, methyl butanoate, methyl isobutanoate, propyl propanoate, ethyl 2-methyl propanoate, methyl pentanoate, heptanoic acid, octanoic acid, 2 ethylhexanoic acid, propyl 3-methylbutanoate, octanols, 4-methyl-3-heptanol, 5-methyl-3-heptanol, 2-ethyl-1-hexanol, dibutyl ether, di-tert-butyl ether, dibutylamine, diisobutylamine, quinoline, isoquinoline, indan, cumene, propylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, mesitylene, o-toluidine, N,N-dimethyl-o-toluidine, nonanoic acid, nonanols, naphthalene, butylbenzene, isobutylbenzene, cymenes, p-diethylbenzene, 1,2,4,5-tetramethylbenzene, decahydronaphthalene, decanoic acid, decanol, 1-methylnaphthalene, carbazole, diphenyl, hexamethylbenzene, dodecanols, diphenyl methane, tridecanols, tetradecanols, hexadecanols, heptadecanols, terphenyls, octadecanols, eicosanols.

14) Compositions according to claim 8 comprising an hydrocarbon charge entering a distillation and/or thermal conversion and/or catalytic conversion plant, such plant being part of a petroleum refinery and/or a petrochemical plant, wherein apparatuses involved are selected preferably from the following group: heat exchangers, columns, reactors, pads, demisters, settlers, tanks, heaters, lines, burners, boilers, drums of any kind.

15) Compositions according to any of the claims 7-14 wherein coke has a different morphology in comparison to that obtained from the same compositions but not containing an additive under present invention.

16) Compositions according to claim 15 comprising at least one swelling agent.

17) Compositions according to claims 15-16 comprising a compound acting as swelling agent, selected preferably from the following group: benzene, toluene, methyl chloride, cyclohexane, nitromethane, nitrobenzene, acetonitrile, carbon tetrachloride, naphthalene, diphenyl, xylene, tetraline, methylcyclohexane, pyridine, methanol, ethanol, ethylenediamine, propanol, 1,4-dioxane, acetone, methylene chloride, chloroform, formamide, aniline, chlorobenzene, o-dichlorobenzene, carbon disulphide, tetrahydrofuran, N,N-dimethylaniline, diethylether, dimethylsulphoxide, acetophenone, dimethylformamide, ethyl acetate, methyl acetate, methylethylketone, 1-methyl-2-pyrrolidone, quinoline.

18) Compositions of vegetable diesel fuel which give raise to: i) minor gaseous emissions and/or ii) reduction in particulate and/or soot and/or SO<sub>x</sub> and/or NO<sub>x</sub> and/or PAH emitted during combustion and/or iii) minor burner and combustion apparatuses fouling and/or iv) minor CCR and/or v) minor engine deposits.

19) Compositions of vegetable diesel fuel according to claim 18 comprising an additive selected preferably from the group of claim 4.

20) Compositions according to claim 19 comprising an additive according to claim 5,6.

21) Additive according to claims 19-20 comprising compounds with boiling point in the range 200-500 °C, preferably 300-400 °C, selected from the following group:  $\beta$ -antraquinoline, anthraquinone, antipyrine, eicosanol, benzalacetophenone, 2-nitrobenzamide, benzanthracene, 1-chloro-2,6-dinitrobenzene, hydroquinone, p-dinitrobenzene, 1,3,5 trimethyl-2,4 dinitrobenzene, dodecylbenzene, hexachlorobenzene, hexaethylbenzene, hexamethylbenzene, nonylbenzene, 1,2,3-triaminobenzene, 1,2,3-trihydroxybenzene, 1,3,5-triphenylbenzene, p-benzidine, benzyl, 1-methylbenzimidazol, 2-benzoylbenzofuran, benzoic anhydride, 2-benzoyl-methyl benzoate, benzyl benzoate, 4-tolyl benzoate, 2-phenoxybenzoic acid, benzoine, benzophenone, 4,4'-bis(dimethylamino), 4-chlorobenzophenone, 4,4' chlorobenzophenone, 2,2'-dihydroxybenzophenone, 2,2'-dimethylbenzophenone, 4,4'-dimethylbenzophenone, methylbenzophenone, 1,2 benzopyrene,  $\beta$ -naphthoquinoline, 2-methyl- $\beta$ -naphthoquinoline, 2-hydroxybenzothiazol, 2-phenylbenzothiazol, 2-amino benzylic alcohol, 3-hydroxy benzylic alcohol,  $\alpha$ -1-naphthyl benzylic alcohol, benzyl-ethyl-phenyl-amine, benzylaniline, benzyl ether, phenylacetophenone, 2-acetamide diphenyl, 2-amino diphenyl, 4,4'-bis(dimethylamino) diphenyl, diphenol, dianisol, butyl-bis(2-hydroxyethyl)amine, butylphenylamine, butylphenylketone, carbamic acid, carbazol, 1,2,3,4 tetrahydrocarbazol, diphenylcarbonate, cetyl alcohol, cetylamine, cinnamic acid, benzylcinnamate, coronene, coumarine, lindan, dicarboxylic acid of cyclohexane, dibenzofuran, dibenzothiophene, dibenzylamine, diethylene glycol dibenzyl ether, diethylene glycol monolaurate, diethylene glycol (2-hydroxypropyl) ether, diethylenetriamine, di- $\alpha$ -naphthylamine, di- $\alpha$ -naphthylamine methane, di- $\beta$ -naphthylamine, dioctylamine, diphenylamine, diphenyl disulphate, 4,4'-diamino diphenyl, 4,4'-dimethylamino diphenyl, 4-hydroxy diphenyl, diphenyl methanol, diphenyl ethylamine, diphenylsulphide, di-( $\alpha$ -phenyl ethyl)amine, di-isopropanolamine, di-2-tolylamine, 4,4' ditolylsulphate, eicosanol, 1,1,2 triphenylthane, ethylene glycol 1,2 diphenyl, ethyl-di-benzylamine, ethylene glycol monobenzyl ether, ethylene glycol monophenyl ether, fluorene, N,N-diphenylformamide, phenylformamide, tolylformamide, 2-benzoylfuran, 2,5 diphenylfuran, glycerol and related esters, eptadecylamine, eptadecanol, cerilic alcohol, hexadecanamine, hydroxyethyl-2-tolylamine, triethanolamine, imidazole, methylimidazole, phenylimidazole, 5-amino-indane, 5-esyl-indane, 1-phenyl-1,3,3-trimethyl-indane, indanole, indazole, 2,3 diphenyl-indene, indole, 2,3 dimethyl-indole, triptamine, 2-phenyl-indole, isocoumarine, isonicotine, diethyl-isophthalate, isoquinoline, benzyl laurate, phenyl laurate, lauryl alcohol, lauryl amine, lauryl sulphate, diethyl-benzyl-malonate, melamine, diphenyl methane, triphenyl methane, 4-benzyl-morpholine, 4-phenyl-morpholine, 4-(4-tolyl)-morpholine, myristic alcohol, 9,10-dihydro-naphthacene, acetyl-naphthalene, benzyl-naphthalene, butyl-naphthalene, chloronitro-naphthalene, dihydro-naphthalene, dihydroxy-naphthalene, dinitro-naphthalene, methyl-naphthalene, nitro-naphthalene, phenyl-naphthalene, naphthoic acid, naphthol, naphthylamine, methyl-naphthylamine, naphthylphenylamine, naphthylsulphide,  $\alpha$ -naphthyl-2-tolyl-ketone, methyl or ethyl ester of nitrobenzoic acid, 3-nitrobenzamide, nonacosanol, octadecanol, octyl-

- phenyl-ether, pentadecylamine, pentadecanol, phenanthrene, hexahydrophenanthrene, octahydrophenanthrene, phenanthroline, phenanthroquinone, phenazine, 3-hydroxyacetophenone, 2-benzylphenol, p-cycloesylphenol, m-phenylphenol, phenothiazine, 4-hydroxyphenylacetonitrile, o-phenylenediamine, N-phenyl-phenylenediamine, 4-methyl-phenylenediamine, diphenyl ether, bis-(2-phenyl ethyl)amine, phenylhydrazine derivatives such as benzoyl, sulphide, sulphone and sulfoxide, phosphine derivatives such as phenyl, triphenyl and oxide, triphenylphosphite, acid esters such as dibutyl, dibenzyl, diethyl and diphenyl, phthalic anhydride, 3,5 dichloro phthalic anhydride, N-benzoylpyperidine, 1,3-diphenoxypropane, N-(2-tolyl)propionamide, 1-methyl-3-phenyl-pyrazoline, pyridine derivatives such as 3-acetamido, 3-benzyl, 4-hydroxy, 2-phenyl, pyrogallol, catechol, quinazoline, quinazolinone, quinoline and its derivatives such as 2-amino-4-methyl, 4-amino-2-methyl, 5-amino, 2-hydroxy-4-methyl, 6-hydroxy, 8-hydroxy, 2-phenyl, resorcine, 4-esylresorcine, retene, salicylic acid and related benzylic e methyl esters, phenylsuccinic anhydride, succinimide, N-benzylsuccinimide, N-phenylsuccinimide, tartaric acid esters such as dibenzyl and dibutyl, o-terphenyl, m-terphenyl, 1,14 tetradecandiol, tetradecanol, tetraethyleneglycol, tetraethylenepentamine, 2,4-diphenyl thiazole, 2-methyl-5-phenyl thiophene, tetraphenyl thiophene, 2,5-diaminotoluene, 3,5-dihydroxytoluene, 4-phenyl toluene, p-toluensulphonic acid and related methyl and propyl esters, o-toluic acid and related anhydride, N-benzyl-toluidine (o-, m- e p-), 4-tolyl-sulphone, 1,2,4 od 1,2,3 triazole, tribenzylamine, tributylamine, triethanolamine, triethyleneglycol and related monobutylether, triethylamine, trioctylamine, triphenylamine, trithiane, tritanol, 2-pyrrolidone, xanthene, xanthone, nitroxyls, xylidine.
- 22) Compositions according to claim 1 comprising additives in aqueous and/or vapour phase to favour decoking and/or cleaning and/or reclaiming of apparatuses containing hydrocarbon and/or petroleum products and/or fuels contaminated materials, included when such decoking and/or cleaning and/or reclaiming are made preferably without taking said apparatuses out of service.
- 23) Compositions according to claim 22 wherein apparatuses are selected preferably from the following group: petroleum refining and/or petrochemical plants, flottators, API separators, desalters, heat exchangers, heaters, demisters, columns, lines, tanks, pads, reactors, settlers, drums of any kind.
- 24) Compositions according to claim 22 wherein compounds are selected preferably from the following group: aminoethanol, acetaldehyde, acetamide, acetic acid, ethyl acetate, acetone, acetonitrile, ethyl glycinate, amino benzoic acid, antipyrine, chlorobenzaldehyde, catechol, resorcinol, hydroquinone, benzyl alcohol, benzylamine, butylamine, dimethylglycol, butyl alcohol, methylethylketone, methylvinylketone, butyl aldehyde, butyrolactone, caprolactam, cyclohexylamine, cyclohexanol, dibutylamine, diethyleneglycol and related ethers mono- and di-butyl, mono- and di-ethyl, 1,3 and 1,4 dioxane, dipropylamine, ephedrine, ethyleneglycol, ethanol, ethanolamine, ethylenediamine, benzyl cellosolve, butylcellosolve, methylcellosolve, ethylcellosolve, formaldehyde and related diethyl-, dimethyl- and dipropyl-acetals, benzoylformaldehyde, formamide, N,N diethyl and N,N dimethylformamide, formic acid, tetrahydro-2-furanone, glycerol, hexamine, hexamethylenediamine, hexamethyleneglycol, triethanolamine,

- diethanolamine, imidazole, methanol, dimethylsulphoxide, morpholine, naphthalensulphonic acid, naphthoquinone, pycoline, pyperazine, piperidine, propylamine, propylen glycol, propanol, propionamide, pyrazine, pyridazine, pyridine, pyrogallol, 2-pyrrolidone, N-methyl-2-pyrrolidone, quinazoline, quinoxaline, tetraethyleneglycol, p-toluensulphonic acid, triethylamine, glycerol derived as a by-product of fatty acids transesterification (with or without dissolved fatty acid and/or alcohol (GCAG or GSAG)), any glycerol derived as a by-product of industrial activities (e.g. the ones derived from the production of soap and/or fatty acids).
- 25) Compositions according to claim 1 comprising compounds of the hydrogenation catalyst type, selected preferably from organometallic compounds of the following metals: molybdenum, cobalt, iron, nickel; wherein said compounds are parts of additives under present invention, such that their final concentration in the compositions is from 0.0001 to 0.9 ppm in weight as metal.
- 26) Compositions according to claim 25 wherein said organometallic compounds are prepared from reaction between an inorganic compound and a compound under present invention, preferably of the acidic type.
- 27) Compositions according to claim 26 wherein compositions are preferably selected from the following group: i) a reaction product between a molybdenum compound selected from the group:  $\text{MoCl}_3$ ,  $\text{MoCl}_2$ ,  $\text{Mo}_2\text{O}_3$ ,  $\text{MoO}_2$ ,  $\text{Mo}_2\text{O}_5$ ,  $\text{MoP}_2$ ; and an acidic type compound selected from the group: GCAG, fatty acids, carboxylic acids, any acid vegetable and/or animal and/or industrial oil derived as a by-and/or waste-product of industrial activities (e.g. crude and/or distilled tall oil, castor oil, tallow oil, acid seeds oil, acid olive oil, etc.); ii) a molybdenum compound selected from the group:  $\text{Mo}(\text{CO})_6$ ,  $\text{MoO}_2\text{Cl}_2$ ,  $\text{Mo}_2\text{O}_3\text{Cl}_6$ ,  $\text{MoO}(\text{OH})_2\text{Cl}_2$ , dissolved in a compound selected from the group of claims 4,5,6.
- 28) Hydrocarbon and/or fuel, included coke and/or coal, and/or additives compositions according to claim 1 which give rise to: i) improved combustion efficiency and/or ii) minor gaseous emissions and/or iii) reduction in particulate and/or soot and/or  $\text{SO}_x$  and/or  $\text{NO}_x$  and/or PAH emissions generated during their combustion and/or iv) reduced burner and/or combustion apparatuses fouling, included heater and/or boiler internal, such to make minor blowings.
- 29) Compositions according to claim 28 comprising an additive selected from the group of claim 4.
- 30) Compositions according to claim 29 comprising an additive according to claim 5,6.
- 31) Additive compositions according to claim 28 comprising compounds that are insoluble but dispersible in oil phase, preferably a hydrocarbon phase, and wherein boiling point of said compounds is preferably  $> 100^\circ\text{C}$ , and wherein said compounds are selected preferably from the following group: glycerol, MEA, DEA, TEA, succinimide, GCAG, GSAG, 2,3-dimethoxyaniline, 2-antraquinonsulphonic acid, 2-aminobenzamide, benzenesulphonic acid, benzimidazole, benzofuran, dipyrilidil, putrescine (1,4 diaminobutane), butantriol, 2-caprolactone, cyclodecanol, diethyleneglycol dibenzylether, triazoethanol, N-3-tolyl-formamide, 1,2,3,4,5,6 hexanesol, hydantoin, hydroquinone dibenzoate, hexacarboxybenzenic acid, ethylmyristate, 2-amino-3-chlorophenol, 2-amino-3-nitrophenol, diaminophenol, 4-methyl-o-phenylendiamine, triethylphosphine

- sulfide, isobutylpyperidine, N-(2-hydroxyethyl)piperidine, 3-methylpyperidine, 1,3-diamino-2-propanol, 5-chloro-3-methyl-pyrazol, 3-methyl-1-phenyl-5-pyrazolinone, 2,4- or 3,5-diaminopyridine, 4-hydroxypyridine, methylpyrimidine, 8-aminoquinoline, resorcinol monobenzyl ether, succinic acid monomethylester, o-tolylacetic acid, 1,2,3 or 1,2,4 triazol, triisopropanolamine.
- 32) Additive compositions according to claim 31 wherein compounds are injected directly in the oil phase and/or dispersed in oil phase via a suitable emulsifier and/or injected in a suitable solvent and then dispersed in oil phase via a suitable emulsifier.
- 33) Compositions according to claim 32 comprising compounds which give rise to "micorexplosions", wherein such compounds are selected preferably from the following group: 2,3,4 trinitroanisole, 1,3,5-trimethyl-2,4-dinitrobenzene, 1,3,5-trimethyl-2,4,6-trinitrobenzene, benzohydroxamic acid, 2,4,6-trinitro-m-cresol, nitroglycerol, 1,3,6,8-tetranitronaphthalene, 1,3,5-trinitronaphthalene, 2,5-dihydroxy-3,6-dinitro-p-benzoquinone, 2,4,6-trinitrophenol (pyric acid), trinitrotoluene, trinitroacetonitrile, 2,3,5-trinitro-p-xylene, substituted triazoles and/or tetrazoles with 0-2 hydrocarbonyl substituents C<sub>1</sub>-C<sub>20</sub>.
- 34) Fuel compositions according to claim 1 which give rise to i) minor carbon residue and/or ii) minor particulate and/or soot and/or SO<sub>x</sub> and/or NO<sub>x</sub> and/or PAH emissions and/or iii) minor engine fouling and/or deposits and/or iv) improved thermal stability and/or v) improved oxydation stability.
- 35) Fuel compositions according to claim 34 comprising an additive selected from the group of claim 4.
- 36) Compositions according to claim 35 comprising an additive according to claim 5,6.
- 37) Fuel compositions according to claims 34 - 35 wherein the fuel is selected preferably from the following group: diesel fuel, fuel oil, jet fuel, gasoline, naphtha, kerosene, bunker oil.
- 38) Additives compositions according to any of the claims 1-37 comprising suitable amounts of dispersants selected preferably from the following group: a) substituted amines, where the substituent is an hydrocarbon containing at least 8 carbon atoms; b) acylated compounds containing nitrogen and having a substituent with at least 10 aliphatic carbon atoms, such substituent being obtained by reaction of an acylant carboxylic acid with at least an amminic compound containing at least a group -NH-, said acylant agent being joined to said amminic compound by way of a imido, amido, amidine or acyloxyammonium bridge; c) nitrogen containing condensated compounds of a phenol, an aldehyde and an aminic compound, having at least a group -NH-; d) esters of a substituted carboxylic acid; e) hydrocarbonyl substituted phenols; f) alcoxylated derivatives of an alcohol, a phenol or an amine; g) polymetacrylates; h) polyisobutylene succinimide; i) polyisobutylene succinate; j) alkylaryl-sulphonates; k) alkanolamin-alkylaryl-sulphonates; l) alkylaryl-sulphonic acids.
- 39) Additives compositions according to any of the claims 1-38 which give rise to i) improved solvency of asphaltenic molecules and/or ii) penetration of polar compounds inside asphaltenic molecules, said polar compounds having preferably a low molecular weight (up to 400) and being preferably of the saturated type and/or iii) resin solubilization and their subsequent delocalization.

- 40) Application of additives compositions according to claim 4 for limiting asphaltenes fouling in crude oil extraction processes, as well as in crude oil refining processes, and/or for the purposes of: a) emulsion breakers assistants; b) controllers of oil/water interface; c) tank sludge cleaners; d) well cleaners (both during production and injection); e) injection systems and water clarification assistants; f) jet pump and orifice cleaners.
- 41) Additives compositions according to claim 40 comprising compositions selected preferably from the group of claims 5,6.
- 42) Crude oil and/or hydrocarbon oil compositions according to any of the claims 1-41 which give rise to minor foaming.
- 43) Application of solvent compositions according to claim 6 for formulating additives under present invention and/or any additive to be utilized in connection with hydrocarbons treatment, said additives being selected from the following group: corrosion inhibitors, neutralizers, antifoulants, antifoamers, emulsion breakers, combustion catalysts, combustion promoters, pour point depressants, CFPP depressants.
- 44) Solvent compositions according to claim 43 comprising i) the absence of compounds of the type: indenenes, indanes, naphthalenes, phenalenes, and/or ii) < 5% content of nitrogen compounds.
- 45) Additives compositions according to any of the claims 1-44 comprising a formulation in the range: solvent 1-99%, active components 99-1%; preferably: solvent 50-90%, active components 10-50%; most preferably: solvent 30-80%, active components 20-70%.
- 46) Additives compositions according to claim 45 wherein dosage, referred to materials to be treated is in the range 1-20000 ppm in weight, preferably 50-8000 ppm, most preferably 100-4000 ppm; and wherein addition temperatures are in the range 1-2000 °C, preferably 1-1300 °C, most preferably 1-900 °C; and wherein addition pressures vary in the range 0.001-15 MPa, preferably 0.01-8 MPa, most preferably 0.1-5 MPa.
- 47) Application of an additive according to claims 4,5,6,15,16,17,21,24,31 for: i) separating organic compounds from solid wastes and/or hazardous wastes (e.g. petroleum waste, refinery sludge, and the like); ii) extracting oil from oil-contaminated catalyst fines, filter aids, drilling cuttings, steel mill waste, bleaching clay, and the like; iii) cleaning filter beds, waste-contaminated soil, and the like; iv) extracting bitumen from tar sands.
- 48) Method for treating compositions under present invention, such that they create i) reduced fouling and/or ii) reduced coke formation in the apparatuses they flow and/or are contained and/or iii) increased conversion yields and/or iv) reduced coke formation on catalysts and/or v) reduced gaseous and/or particulate emissions, comprising the following steps: a) additivizing the composition with an additive under present invention; b) injecting the additivized composition in an apparatus for use.
- 49) Method according to claim 48 comprising the variations of petroleum refining/petrochemical plants operating conditions, such that is possible to reach supercritical state for utilizing, in said conditions, any of the compounds under present invention.

- 50) Application of an additive and/or a compound according to claims 4,5,6 to modify emulsion breakers formulations.
- 51) Application according to claim 50 wherein the additive under present invention is 1-40%, preferably 1-30%, most preferably 1-20% of final emulsion breaker formulation.
- 52) Application of an additive according to any of the claims 1-50 to pretreat a petroleum refining/petrochemical plant charge, included the pretreatment to a catalytic plant to achieve a better penetration of the charge in the catalyst in plant selected preferably from the following group: Catalytic Hydrocracking, Residue Demetallation, Reformers, Fluid Catalytic Cracking, and the like.
- 53) A process for inhibiting fouling of apparatuses in chemical processing or oil refining processing comprising incorporating into a petroleum derived stock an effective amount of a composition under present invention.
- 54) Method for preventing stability and/or incompatibility and/or HFT and/or CCR problems of crude oils, fuel oils, bunker oils, and mixture thereof, comprising incorporating into said oils an effective amount of a composition under present invention.
- 55) Application of an additive according to any of the claims 1-50 as cleaner or deposit inhibitor in a fuel for an internal combustion engine.
- 56) Application of any by-product and/or any waste product deriving from any process, already known or to be implemented, that contains any compound, and mixture thereof, under the present invention, for formulating compositions under present invention.
- 57) Process for reducing sulphur contained in heavy compounds, coke included, obtained in petroleum refining/petrochemical plants, comprising the following steps: a) additivizing the plant charge with an additive under present invention; b) charging the additivized plant charge in a plant for processing.
- 58) Additives compositions according to claim 57 selected preferably from the group of claim 4.
- 59) Additives compositions according to claim 58 selected preferably from the group of claims 5,6.
- 60) Application of additives compositions according to any of the claims 1-59 to decrease hydrogen make of FCC catalysts.
- 61) A method for cleaning and/or degassing apparatuses according to claims 4,5,6,22,23,24, comprising the following steps: a) adding an additive composition under the present invention to a medium for dispersing and/or solubilizing it (e.g. water, steam, naphtha, gas oil, etc.); b) circulate the solution of step a) into the apparatus to be cleaned; c) repeat step a) and b), after discharging the solution of step b), until the solubilized hydrocarbon content in the solution is held constant.
- 62) Any new and novel feature hereinbefore described, or any new and novel combination of hereinbefore described features.

1/1

## SIMULATED DISTILLATION RESULT

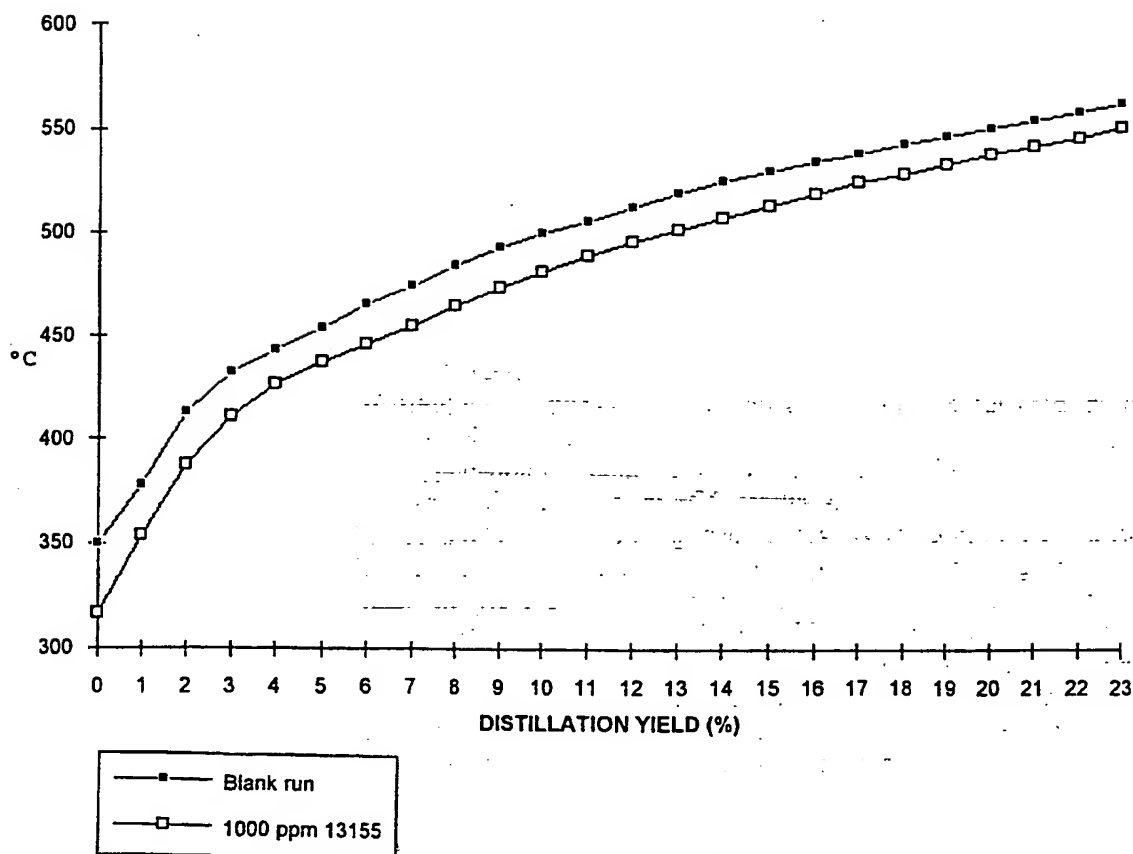


Figure 1